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Assessment of Techniques for Measuring Tropospheric N_xO_y

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Proceedings of a workshop sponsored by the NASA Office of Space Science and Applications and NASA Langley Research Center and held in Palo Alto, California August 16-20, 1982

25th Anniversary
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Assessment of Techniques for Measuring Tropospheric N_xO_y

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NASA
National Aeronautics and Space Administration

Scientific and Technical Information Branch

1983

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PREFACE

The National Aeronautics and Space Administration, through its Tropospheric Chemistry Program, has sought and utilized the advice of the scientific community in the formulation of its research efforts. The NASA Working Group on Tropospheric Program Planning, led by Dr. John Seinfeld, established a foundation to guide program development (NASA RP-1062, 1981). One of four areas recommended for expanded activities was instrument development, which is aimed at improving our capability to measure the important trace gases and aerosols which are the key species in the major atmospheric biogeochemical cycles. To assist in guiding our utilization and development of instrumentation and to focus more clearly on specific needs, the Instrument Workshop for N_xO_y Tropospheric Species was conducted in Palo Alto, California, August 16-20, 1982. The workshop participants were asked to provide assessments of existing sensors and of new technologies deemed to have potential for measuring N_xO_y species at levels characteristic of the nonurban troposphere.

The availability of adequate instrumentation is a prerequisite for the implementation of a program to address the pertinent scientific issues of trace constituents within the global troposphere and the factors that control their concentrations. The efforts of this workshop provide meaningful guidance for future instrument developments. The assistance of all who contributed to this workshop is sincerely appreciated. Special thanks are extended to James M. Hoell, Jr., Workshop Chairman; Dieter H. Ehhalt, Coordinator; Fred C. Fehsenfeld, Assistant Coordinator; and Gerald L. Gregory, NASA Rapporteur.

Robert J. McNeal, Manager
Tropospheric Chemistry Program
Office of Space Science and Applications

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PARTICIPANTS

Douglas D. Davis
Georgia Institute of Technology

George A. Dawson
University of Arizona

Dieter H. Ehhalt
KFA, Julich

David W. Fahey
NOAA, ERL

Fred C. Fehsenfeld
NOAA, ERL

Alan Fried
National Bureau of Standards

Gerald L. Gregory
NASA Langley Research Center

Robert C. Harriss
NASA Langley Research Center

William S. Heaps
NASA Goddard Space Flight Center

James M. Hoell, Jr.
NASA Langley Research Center

Barry J. Huebert
Colorado College

James B. Laudenslager
Jet Propulsion Laboratory

William G. Mankin
National Center for Atmospheric Research

Robert J. McNeal
NASA Headquarters

Richard Morrison
Stanford University

John P. Mugler, Jr.
NASA Langley Research Center

Hanwant B. Singh
SRI-International

Arnold L. Torres
NASA Wallops Flight Facility

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EXECUTIVE SUMMARY

The National Aeronautics and Space Administration through its Tropospheric Chemistry Program has sought and utilized the advice of the scientific community in the formulation of its research efforts. The NASA Working Group on Tropospheric Program Planning established a foundation to guide program development (Seinfeld et al., 1981). One of the four areas recommended for expanded activities was instrument development, which is aimed at improving our capability to measure the important trace gases and aerosols which are the key species in the major atmospheric biogeochemical cycles. To focus more clearly on specific needs, the Instrumentation Workshop for N_xO_y Tropospheric Species was conducted in Palo Alto, California, August 16-20, 1982. The objectives of this workshop were

1. To provide an assessment of the capability of existing sensors of N_xO_y species at levels characteristic of the nonurban troposphere

2. To identify those techniques adaptable to real-time measurement (sampled or continuous) onboard an aircraft platform

3. To address the concern for intercalibration and intercomparison of techniques for measuring specific species

4. To recommend promising technologies for research and development for measuring important species for which a capability does not now exist or is presently of inadequate sensitivity

Workshop attendees included approximately 15 invited participants from government, universities, and industry. Each participant was selected based on a demonstrated expertise in either the development or application of N_xO_y monitoring techniques for global tropospheric research.

As input into the workshop, NASA prepared an overview of its current Global Tropospheric Program, highlighting ongoing activities as well as long-range plans. Included in these discussions was a brief summary of N_xO_y species chemistry in the troposphere and required measurement capabilities for various N_xO_y species. These measurement capabilities (horizontal and vertical spatial resolution and required concentration levels), combined with the experiences of the workshop participants, became the basis for discussion of the various techniques. This workshop report is a summary of those discussions and written material prepared by the participants to describe the techniques discussed.

The species discussed in this workshop document include NO, NO_2, NO_3, NO_3^- aerosol, HNO_2, HNO_3, HNO_4, PAN, and N_2O_5. Techniques are classified into six basic categories, depending on the detection principle. These are chemiluminescence, laser-induced fluorescence, ionization spectroscopy, absorption spectroscopy, photothermal spectroscopy, and "grab sample" type collection techniques. Many techniques are discussed in each category. For each N_xO_y species measurement technique, an assessment is made of the current measurement capabilities in each of ten areas: (1) current status of availability (i.e., design concept to operational), (2) sensitivity, (3) time resolution or response, (4) accuracy, (5) precision, (6) interferences, (7) concentration at which a technique has been calibrated, (8) environmental constraints, (9) available sampling platforms, and (10) any additional comment or information important to assessing the capability of a given technique.

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Techniques discussed in the document are at various stages of development, ranging from concepts (on paper only) to operational in-the-field instruments. For techniques existing as a concept or as laboratory instruments, discussion focused on anticipated measurement capabilities and future research and/or hardware development required to obtain anticipated capabilities. For operational techniques, discussion focused on current capabilities, known instrument interferences and shortcomings, and research required to improve instrument capabilities. Current and projected measurement capabilities are compared to required global measurement needs to identify species for which measurement capabilities are inadequate (now and future). A brief description of each technique discussed at the workshop is included in the document.

Conclusions, observations, and the consensus of opinion arising from the workshop are briefly noted in the following summary material.

1. For NO, various measurement techniques are being developed and should provide adequate and demonstrable tropospheric measurement capabilities by 1984. Programmatic interest and scientific need are sufficient to ensure that NO techniques will progress and mature to an operational status. In addition, techniques being developed employ different detection principles, ranging from chemiluminescence to laser-induced fluorescence.

2. For species like NO_2, HNO_3, PAN, and NO_3^- aerosol, current measurement capability is not adequate for global tropospheric needs. However, several techniques are under development, and such techniques may prove adequate after 2 or 3 more years of development and testing. Although the development of instruments is not being directed (funded) by well-defined programmatic needs, the general interest in these species combined with pressure from the scientific community will provide an emphasis to complete development and testing. It is noted that only a few techniques are being considered for HNO_3, PAN, and NO_3^- aerosol, and as such, perhaps other approaches should be considered.

3. For species such as NO_3 and HNO_2, measurement techniques are not actively being developed to meet global tropospheric needs. Without additional programmatic support and/or strong scientific pressure, techniques for these species will lag in development. Again the need for pursuing techniques using various detection principles is noted. For these species (because of lack of interest or need) little emphasis has been placed on new starts or fresh ideas. The techniques being considered are sound, attractive approaches but are basically spin-offs or tangents of techniques used to measure the other N_xO_y species, such as NO, NO_2, and HNO_3.

4. For N_xO_y techniques currently being developed, several areas of technology were identified which would improve existing capabilities of these techniques. Briefly, these areas are: (a) more efficient photon collection and detection systems; (b) more specific converters (e.g., chemiluminescence systems use converters to convert NO_2, HNO_3, or PAN to NO before detection); (c) higher repetition rate lasers; (d) more field-hardened lasers; (e) more choice of available laser frequencies; and (f) more reliable and industry acceptable calibration standards and procedures (i.e., most gas standards are a factor of 10^3 to 10^6 higher than concentrations being measured). The need for opportunities to field-intercompare techniques being developed for the same species was also identified.

5. Two fundamental research or basic technology areas are currently limiting development of N_xO_y (as well as other species) measurement techniques. Both are areas requiring general research independent of specific species. The first is calibration standards and procedures. Preparation of standards and associated procedures

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are currently limited to only the ppmv level, and have been for the last 5 years. The lack of technology to prepare, stabilize, and furnish certified standards at ppbv (better yet, pptv) levels is recognized as a major obstacle in instrumentation development. The lack of any recognized standards (at any reasonable concentration) for the more reactive species like HNO_3 and PAN is an additional obstacle. Until reliable standards and calibration procedures are developed and agreed upon by the scientific community, the full potential and application of many current and future N_xO_y measurement techniques will not be realized. Existing techniques with known artifact, background, or interference effects can be improved if lower concentration standards are available and are incorporated into measurement schemes. The second basic research area is laser development. Improved laser technology resulting in improved capabilities, more rugged environmental conditions, more options on wavelength choice, and more suitability for field operation would allow researchers to maximize their instrument performance from the very first design choice, that of the laser. Currently, these choices are frequently based on what is available and have been shown to operate well in the past.

In terms of measurement validation, another major topic discussed at the workshop, it was determined that more emphasis must be placed on calibration and intercomparisons. In the final analysis, the criterion by which the accuracy of the measurement of an atmospheric compound is established is intercomparison of measurements made by instruments using different principles of detection. Such measurements should be carried out in the field and subjected to a wide variety of atmospheric concentrations. Prerequisites for field intercomparisons are instrument calibrations using validated procedures and traceable standards. A significant goal of tropospheric research efforts should be to validate the critical measurements of N_xO_y compounds.

INTRODUCTION

In its continuing efforts to direct its applications programs toward relevant national needs, NASA is conducting the Tropospheric Chemistry Program, the long-range objective of which is to apply NASA's space technology to assess and predict human impact on the troposphere, particularly on the regional to global scale. The increasing importance of pollution on these scales and the synoptic view afforded from satellites suggest that space observations can play a unique and critical role toward satisfying the objective. A NASA-sponsored working group of scientists prepared an overview of the scientific problems that need to be addressed in order to understand the large-scale troposphere (Seinfeld et al., 1981). The group recommended that NASA undertake expanded efforts to develop space applications for tropospheric air quality monitoring in the areas of instrument development, modeling, laboratory studies, and field measurement activities.

To help NASA in formulating a detailed implementation plan, assistance has been sought from workers in this field to identify the high-priority research required in each of the four program components. Such studies included specific regional scientific concerns (Levine and Schryer, 1978), the results from and the needs of tropospheric modeling (National Aeronautics and Space Administration, 1981), multiphase processes, including heterogeneous catalysis (Schryer, 1982), and passive remote sensing (Keafer, 1982).

This volume reports the results of the Instrumentation Workshop for N_xO_y Tropospheric Species. The workshop was sponsored by the NASA Office of Space Science and Applications and conducted under the direction of the Global Tropospheric Experiment

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Project Office of NASA Langley Research Center. The support of The Bionetics Corporation, and particularly the assistance of Howard J. Curfman, Jr., and Helen Ann Thompson, is gratefully acknowledged.

OBJECTIVES AND ORGANIZATION

The objectives of the workshop were

1. To provide an assessment of the capability of existing sensors of N_xO_y species at levels characteristic of the nonurban troposphere

2. To identify those techniques adaptable to real-time measurement (sampled or continuous) onboard an aircraft platform

3. To address the concern for intercalibration and intercomparison of techniques for measuring specific species

4. To recommend promising technologies for research and development for measuring important species for which a capability does not now exist or is presently of inadequate sensitivity

The organization and planning of the workshop was conducted under the direction of the Global Tropospheric Experiment (GTE) project instrument scientist, who served as workshop chairman. A coordinator and an assistant were responsible for actually conducting the workshop, including the discussion sessions and the documentation planning and assignments. A NASA rapporteur coordinated the writing assignments and assisted the chairman and coordinators in the preparation of this report. The workshop and this documentation are a collaborative effort of the following participants:

James M. Hoell, Jr., Workshop Chairman
Gerald L. Gregory, NASA Rapporteur
Dieter H. Ehhalt, Coordinator
Fred C. Fehsenfeld, Assistant Coordinator

Douglas D. Davis
George A. Dawson
David W. Fahey
Allen Fried
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Barry J. Huebert
James B. Laudenslager
William G. Mankin
Richard Morrison
Hanwant B. Singh
Arnold L. Torres

MEASUREMENT REQUIREMENTS FOR N_xO_y TROPOSPHERIC SPECIES

The nitrogen family is but one of the important chemical cycles that must be considered if global tropospheric chemistry and/or circulation are to be investigated. Nitrogen oxide (N_xO_y) species, a subgroup of the nitrogen family, are hypothesized to play a critical role in tropospheric photochemistry, particularly through coupling with the H_xO_y cycle to modulate OH levels. The principal reactive N_xO_y species found in the lower atmosphere include NO, NO_2, and HNO_3. These species are coupled chemically by reactions such as:

$$NO + HO_2 \rightarrow NO_2 + OH$$

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$$NO_2 + OH \rightarrow HNO_3$$

After being emitted into the atmosphere, NO can be converted into NO_2; NO_2 reacts with OH to form HNO_3, which is highly soluble and can be removed from the atmosphere by both wet and dry deposition. Several comprehensive discussions of N_xO_y chemistry in the troposphere have been published previously (e.g., Crutzen, 1979; National Aeronautics and Space Administration, 1981).

Verification of existing models of tropospheric photochemistry and important contributions to resolving problems such as the origin of acid rain require accurate data on levels of NO, NO_2, and HNO_3 in remote, nonurban environments. Existing models and measurements indicate that NO levels in remote marine air are in the 1- to 10-pptv range (e.g., McFarland et al., 1979). Nitric acid vapor can also drop below 10 pptv in the remote marine boundary layer (Huebert and Lazrus, 1980). Because of the importance of heterogeneous removal of tropospheric nitrogen by wet and dry deposition, it is also important to have accurate techniques for determination of particulate and liquid phase species of nitrogen. The capability to measure total tropospheric nitrogen has been suggested as an additional useful measurement.

Existing data indicate relatively high variability in N_xO_y species, with sharp gradients from levels of 1 ppmv in urban areas to 1 ppbv in nonurban continental areas to 10 pptv in remote oceanic regions. This high variability combined with the expected application of aircraft sampling platforms suggests the need for emphasis on minimizing sampling times. Ideally, a fast-response system capable of being integrated into a flux measurement program will be required to quantify natural sources and sinks for N_xO_y species. Data in Table I summarize current estimates of instrument sensitivity requirements, spatial sampling requirements, and residence times for major N_xO_y species discussed at this workshop.

Table I - Requirements for N_xO_y Measurements

Species	Residence time	Spatial resolution, km		Detection requirement
		Vertical	Horizontal	
NO	6 sec to 1 day	0.5	200	1 pptv
NO_2	1 sec to 1 day	0.5	200	2 pptv
HNO_2	1 sec to 1 day	0.5	200	1×10^3 cm^{-3}
NO_3	1 sec to 1 day	0.5	200	6×10^5 cm^{-3}
HNO_3	1 hr to 1 week	2	500	1 pptv

DESCRIPTION AND ASSESSMENT OF N_xO_y MEASUREMENT TECHNIQUES

Species and Techniques Considered

Based on the presentation to the workshop by the GTE project scientist on N_xO_y measurement requirements and also on follow-on discussions among members of the N_xO_y workshop, a comprehensive list of N_xO_y species of importance to global tropospheric chemistry was generated. From this list, the group selected which species were (in its opinion) most important, and limited further discussion to those species. These species included NO, NO_2, NO_3, NO_3^- aerosol, HNO_2, HNO_3, HNO_4, PAN, and N_2O_5. Other

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critical nitrogen species, such as ammonia, were identified but were not considered to be within the charter or goals of the N_xO_y instrument workshop. For each of the species considered, measurement techniques were identified and classified into one of four groups according to current status:

Status 1 - technique in a conceptual stage

Status 2 - technique in some phase of laboratory testing

Status 3 - technique ready for field evaluation

Status 4 - technique used successfully in the field

Table II lists the species and respective techniques considered. Each technique is discussed in some detail in this workshop document. Status-1 and -2 techniques are discussed in terms of anticipated instrument development as currently projected by the workshop participants.

Table II - Techniques Considered*

Detection principle	Technique	Species
Chemiluminescence	1) Gas phase titration (O_3)	NO
	2) Converter/gas phase titration (O_3)	NO_2, HNO_3 PAN
Laser-induced fluorescence	1) Single photon	NO
	2) Two photon	NO
	3) Photofragmentation	NO_2, NO_3, HNO_2
	4) Lidar	NO
Ionization spectroscopy	1) Multiphoton ionization	NO, NO_2
	2) Resonant ionization	NO, NO_2
Absorption spectroscopy	1) Fourier transform infrared	HNO_3, PAN
	2) Infrared tunable-diode laser	NO, NO_2 HNO_3
	3) Long path	NO, NO_2, NO_3, HNO_2
Photothermal spectroscopy	1) Photoacoustic	NO_2
	2) Phase fluctuation optical heterodyne	NO_2
Collection	1) Filter	NO_3^-, HNO_3
	2) Condensation	HNO_2, HNO_3
	3) Tungstic acid	NO_3^-, HNO_3
	4) Gas chromatography	PAN

*Two species were discussed (HNO_4 and N_2O_5) for which a measurement technique does not exist for GTE type applications.

Description of Techniques

The material presented in these discussions is a summary of the information supplied by the various workshop participants, including preworkshop, workshop, and postworkshop writing assignments as well as group discussions at the workshop. The material is presented by technique rather than species because many techniques are applicable to more than one N_xO_y species.

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Chemiluminescence Technique

Basic Concept.- As shown in Table II, the chemiluminescence technique is used to detect NO, NO_2, HNO_3, and PAN. (See, e.g., Bollinger, 1982; Kley and McFarland, 1980.) For each application the basic detection principle is based on the use of the chemiluminescent reaction between NO and O_3. Excess O_3 is added to the air sample containing NO, which is passing through a chamber with infrared reflective walls (the reaction vessel). The chemiluminescence is produced by the reaction product NO_2, which is produced in an excited electronic state ($NO + O_3 \rightarrow NO_2^*$) and subsequently relaxes by photon emission. Detection of the NO_2^* becomes a measure of the NO concentration in the sample. In applications other than NO detection, the air sample is first preconditioned to convert the species of interest (NO_2, HNO_3, or PAN) to NO prior to reaching the reaction vessel. Signal differencing between samples before and after preconditioning accounts for initial NO concentrations in the air sample. The broad emission spectrum of NO_2^* produced in the $NO-O_3$ reaction begins at approximately 600 nm, extends beyond 3000 nm, and is centered at 1200 nm. Competing with photon emission is collisional quenching of NO_2^*. In high-sensitivity systems, detection of emitted photons is by a cooled, red-sensitive photomultiplier tube operated in a pulse-counting mode. A filter is used to block radiation below 600 nm to prevent interfering signals from ozonalysis of other materials. A mass flow controller is often used to stabilize the sample flow (and hence the magnitude of collisional quenching of NO_2^*) during altitude changes (aircraft application) and the reaction vessel pressure is regulated at about 10 torr. Assuming that NO and O_3 are well mixed in the reaction vessel, that there is an excess of O_3, and that the flow control is functioning properly, a steady-state analysis of chemistry and transport for NO in the reaction vessel can be performed which will result in a photon production rate proportional to the NO concentration in the air sample. Careful design of the reaction vessel to achieve efficient mixing of O_3 and NO close to the photomultiplier tube (PMT), high collection efficiency, and high sample flow rates allow state-of-the-art (compared to off-the-shelf) instruments to achieve sensitivities of 4500 counts/sec for 1 ppbv NO. These sensitivities agree well with those calculated from theoretical considerations.

The detection limit of the chemiluminescence technique is determined by the background against which the measurements are made. This background is due in part to the dark current of the photomultiplier tube ($\approx$200 counts/sec when cooled to $\leq$230 K) and also to an additional 100 counts/sec associated with ozone flow in the system. This establishes a detection limit of about 17 counts/sec for the species of interest. In addition to this background, artifact signals are observed (magnitude and type are dependent on the N_xO_y species being detected). These artifacts are not attributed to interferants in the ambient air stream, but rather to instrument configuration, cleanliness, and/or contaminants. For example, in the NO measuring mode this signal can amount to 40 to 50 counts/sec and is often associated with contamination due to exposure of the system to high concentrations of condensible organic vapors. In order to correct for background (other than dark current) and artifacts, zero mode and calibrations are incorporated into the instrument measurement cycle.

Aside from the background and artifact signals, the possibility exists that chemical species in the atmosphere other than the N_xO_y species of interest may cause a chemiluminescent response in the instrument or modify the sensitivity of the instrument.

NO Species Detection.- For ambient NO measurements, the theoretical detection limit of the technique is approximately 4 pptv for a 1-sec sample time and is obtained from a background detection limit of 17 counts/sec (signal/noise = 1) and a

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detector sensitivity of 4500 counts/sec for 1 ppbv NO concentration. State-of-the-art systems designed to measure and account for background and artifact signals have detection limits of less than 10 pptv. Artifacts associated with the NO measurement are mostly system cleanliness parameters, which are related to system exposure to high concentrations of condensible organic vapors and/or high concentrations of NO. Artifact signals of 10 to 30 pptv are common and are accounted for in the measurement cycle through zero air tests and controlled by system cleaning.

Interference possibilities from other compounds in the air include nitrate-containing species such as N_2O_5 or $CH_3C(=O)O_2NO_2$ (PAN) and unsaturated hydrocarbons, which can produce a chemiluminescing product with O_3. Laboratory tests (Bollinger, 1982) indicate that obvious candidate compounds do not have sufficient response in the detector to cause a real-world problem. However, such tests are not all inclusive, and significant interference associated with an unidentified atmospheric compound is always a possibility. There are also compounds which can change instrument sensitivities or backgrounds without producing red photoemission in the reaction vessel. Water vapor is such a compound with a twofold effect. At typical water vapor mixing ratios, H_2O can reduce the detection sensitivity by contributing to the collisional quenching of NO_2* in the reaction vessel and can alter the detection limit by passivating the walls of the reaction vessel, which reduces the red emissions from the walls and decreases the background.

Figure 1 illustrates a typical measurement cycle for a state-of-the-art NO detector. A three-mode cycle is generally used. In the background mode, the counting rate C_B is measured in the absence of NO. In the NO measurement mode the

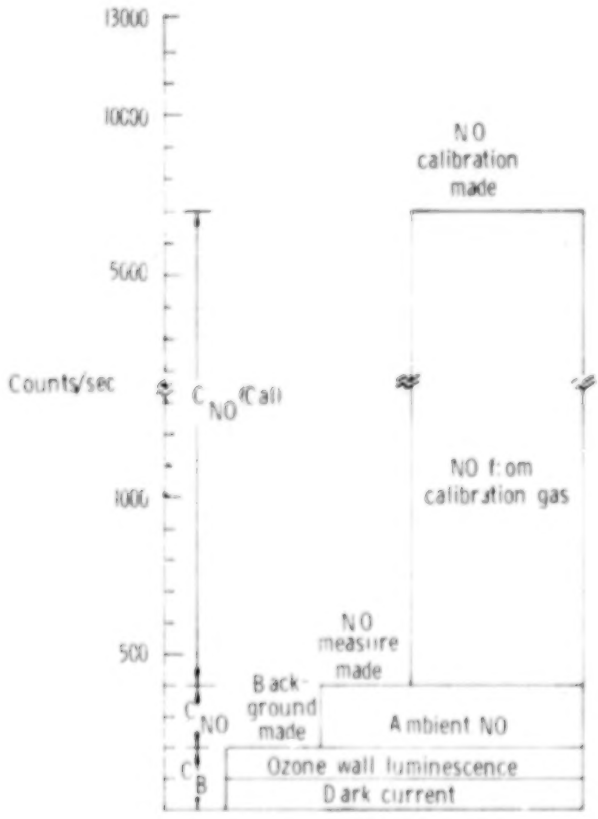

Figure 1.- Measurement cycle for chemiluminescent NO detector.

detector signal consists of a combination of signals associated with the sampled NO (C_{NO}) and the background (C_B). In the NO calibration mode the signal is a combination of the signals associated with the calibration gas $C_{NO}(Cal)$ and the signal recorded in the NO measurement mode. The ambient NO concentration is obtained by mathematically manipulating these measured quantities such that

$$\chi_{NO} = \frac{C_{NO} \cdot \chi_{NO}(Cal) \cdot Q_{NO}(Cal)}{C_{NO}(Cal) \cdot [Q_s + Q_{NO}(Cal)]} \qquad (1)$$

where χ_{NO} = NO concentration in ambient air

$\chi_{NO}(Cal)$ = NO concentration of calibration standard

Q_s = sample flow rate

$Q_{NO}(Cal)$ = calibration standard flow rate

Typically, with $\chi_{NO}(Cal)$ at about 2 ppmv, $Q_{NO}(Cal)$ at 1 to 10 cm^3/sec, and the condition that C_{NO} and $C_{NO}(Cal) \gg C_B$, χ_{NO} can be determined with an uncertainty less than 15 percent at 5 pptv.

NO_2 Species Detection.- For the NO_2 measurement, the sample air stream must first be preconditioned to convert NO_2 in the sample air to NO, which is then detected with the basic detector. Thermal, chemical, and photolytic converters have been used for this preconditioning. Thermal converters (metallic molybdenum beds heated to 200°C) have a conversion efficiency of nearly 100 percent; however, they have the potential to convert nitrogen species (other than NO_2) to NO. Chemical converters ($FeSO_4$ beds) also exhibit nearly 100 percent conversion efficiency but are subject to conversion of other nitrogen species as well as to a decrease in conversion efficiency due to accumulation of moisture within the bed. The photolytic converter (UV radiation source that photodissociates NO_2 to NO), although not believed to significantly convert other nitrogen species, is only about 50 percent efficient. Converter selection and subsequent evaluation are currently major considerations of NO_2 instrument design and operation.

Detection limits for NO_2 are on the order of those for NO (depending on the conversion efficiency). Artifact signals are similar to those for NO, and additional artifacts may be generated by the NO_2-to-NO converter. Interferences are also similar to those for NO and now include those compounds erroneously converted to NO in the converter. The NO_2 measurement cycle is identical to that of figure 1 but uses an NO_2 calibration gas. Accuracy for NO_2 is about 15 percent; however, reasonably high NO concentrations occurring during the day reduce the accuracy of the daytime measurements.

HNO_3 Species Detection.- Measurement of HNO_3 by chemiluminescence relies on the conversion of HNO_3 to NO. A system utilizing the basic NO detector has been field tested (Kelly et al., 1979, 1980). A two-stage converter is used first to convert HNO_3 to NO_2 (thermal converter, quartz tube heated to 375°C) and then to convert NO_2 to NO (chemical converter, $FeSO_4$). Use of an HNO_3 trap (cotton or nylon fiber, loosely packed) permits the employment of a differencing measurement scheme. Calibration of the technique, performed using a standard diffusion cell containing nitric acid, indicates a detection limit of about 0.2 ppbv.

This method for detection of HNO_3 has the same inherent disadvantages associated with the basic chemiluminescence technique, including background, artifacts, and

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potential contributions from unknown interferences. Interference studies show PAN to be a positive interference (i.e., a source of NO_2 via thermal converter) and neither organic amines nor ammonia to be a problem.

Peroxyacetyl Nitrate (PAN) Species Detection.- The chemiluminescence technique has been used to measure PAN during testing of PAN calibration standards at concentrations of 10 to 100 ppbv. In principle, the technique can be applied to PAN ambient measurements, but currently it is limited. The converter used in the PAN calibration standards test, although 100 percent efficient in converting PAN to NO, is not specific to PAN. Until a converter is found which is PAN specific at ambient concentrations, little progress in the development of the technique will occur. In addition, because PAN is a highly reactive species, acceptable calibration standards and procedures do not currently exist. As such, it is not yet possible to consider a multimeasurement cycle, as is currently used in the NO and NO_2 measurement application. It is projected that such a measurement cycle is necessary to satisfy detection limit, precision, and accuracy requirements for ambient measurements. A conventional differencing method involving measurement of NO, NO + NO_2, and NO + NO_2 + PAN is not acceptable.

Assuming the availability of sufficient PAN converters and calibration standards, detection limits and accuracies similar to those stated for NO (i.e., 5 pptv and 15 percent) may be achievable. However, considering the chemical nature of PAN and the technology of the design and use of nitrogen species converters, a real-world projection of detection limit may be on the order of 10 to 20 pptv.

Laser-Induced Fluorescence Technique

The basic laser-induced fluorescence (LIF) approach typically employs one or more pulsed lasers to selectively produce an excited state of the species of interest. If the lifetime of the excited state is short compared to collisional deactivation processes, the excited species will decay to a more stable state in a fluorescent process. This fluorescence generally occurs at UV or visible wavelengths and consequently can be detected on a single-photon basis using high-efficiency photomultiplier tubes and photon-counting techniques. To further enhance the signal-to-noise ratio of the detection process, gated photon-counting techniques synchronized to the pulsed laser are generally employed. The photons emitted in this process can be related to the concentration of the species in the air sample.

The LIF technique is applicable to the measurement of NO, NO_2, NO_3, and HNO_2. Three specific LIF excitation schemes are considered here: single-photon LIF (SP-LIF) and two-photon LIF (TP-LIF), both for NO detection, and photofragmentation LIF (PF-LIF) for NO_2, NO_3, and HNO_2. Of the three techniques, only SP-LIF has been used in the field. TP-LIF and PF-LIF (NO_2 detection) are currently being evaluated in the laboratory, with plans for NASA-sponsored field tests of the TP-LIF technique.

Single-Photon Laser-Induced Fluorescence (SP-LIF).- The general SP-LIF concept for detection of an atmospheric species at ambient pressures is represented in figure 2. The fluorescence-sampling window is positioned on the long-wavelength side of the laser excitation wavelength since the SP-LIF technique is characterized by a red-shifted fluorescence signal component. The sampling window is critical to the success of the SP-LIF technique (when operating at ambient pressures) in that it must be chosen to discriminate against the intense Rayleigh scatter from the laser pump line and also to discriminate against the much weaker, but still significant, Raman scatter signal from the major atmospheric gases such as N_2, O_2, and H_2O. Moreover, the sample window must be chosen to permit measurements in the presence of a

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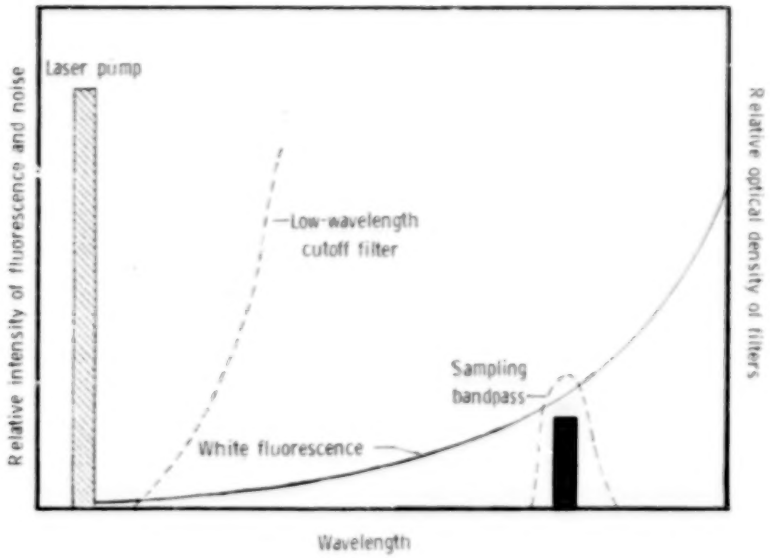

Figure 2.- Single-photon LIF measurement concept.

broadband white fluorescence. The optimum wavelength position of the narrow-bandpass sampling filter is determined from a consideration of the spectral distribution of the white fluorescence noise, from the Franck-Condon factors for both laser pumping and the various possible fluorescence transitions from the excited state, and from the contributions of Rayleigh and Raman scattering. In all cases, the limit of detection of the in situ SP-LIF system will be defined by the white fluorescence noise which exists in the spectral range of the narrow-band filter. The source of this white fluorescence background noise is believed to be a combination of chamber wall fluorescence and fluorescence resulting from atmospheric aerosols.

The specific excitation and detection wavelengths used for NO are shown in figure 3. The $A^2\Sigma^+$ (e.g., $\gamma(0,0)$) transition of NO is excited at 226 nm. The (0,2)

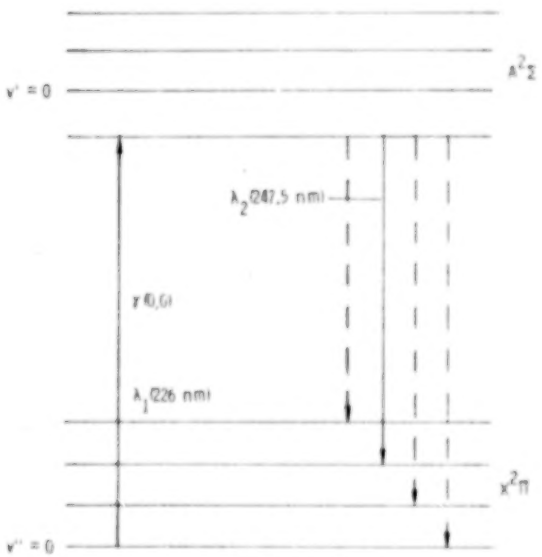

Figure 3.- NO energy diagram for single-photon LIF.

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transition (247.5 nm) of the γ band system has been selected for sampling even though other possibilities exist in the NO energy diagram of figure 3. In this case, detection of the (0,2) transition results in a reduced white fluorescence background signal and also greatly minimizes the interference from ambient SO_2. The SP-LIF technique for detection of NO is discussed in detail in Bradshaw et al. (1982).

Two-Photon (Sequential) Laser-Induced Fluorescence (TP-LIF).- Recall that SP-LIF detection is red shifted with respect to the excitation wavelength. Accordingly, the detection limit of the SP-LIF in situ system is typically defined by the white fluorescence noise illustrated in figure 2. The TP-LIF measurement scheme is characterized by a blue-shifted response with respect to the excitation wavelength. This gives the TP-LIF scheme a major advantage over SP-LIF in that the final fluorescence occurs in a spectral region free from normal noise components. Figure 4 illustrates this for the general case in which two pump lasers, A and B (one in the UV and the second in the visible or IR) are used to excite the molecule of interest to a state that subsequently decays to produce fluorescence in the UV. The white fluorescence generated by both the A and B laser pumping lines is red shifted relative to the fluorescence measurement wavelength. Critical system components for successful application of the TP-LIF technique are a long-wavelength-blocking filter and a rapid-cut-off solar-blind photomultiplier tube (detector). Above all, however, the TP-LIF scheme can only be employed on molecules possessing two bound excited states.

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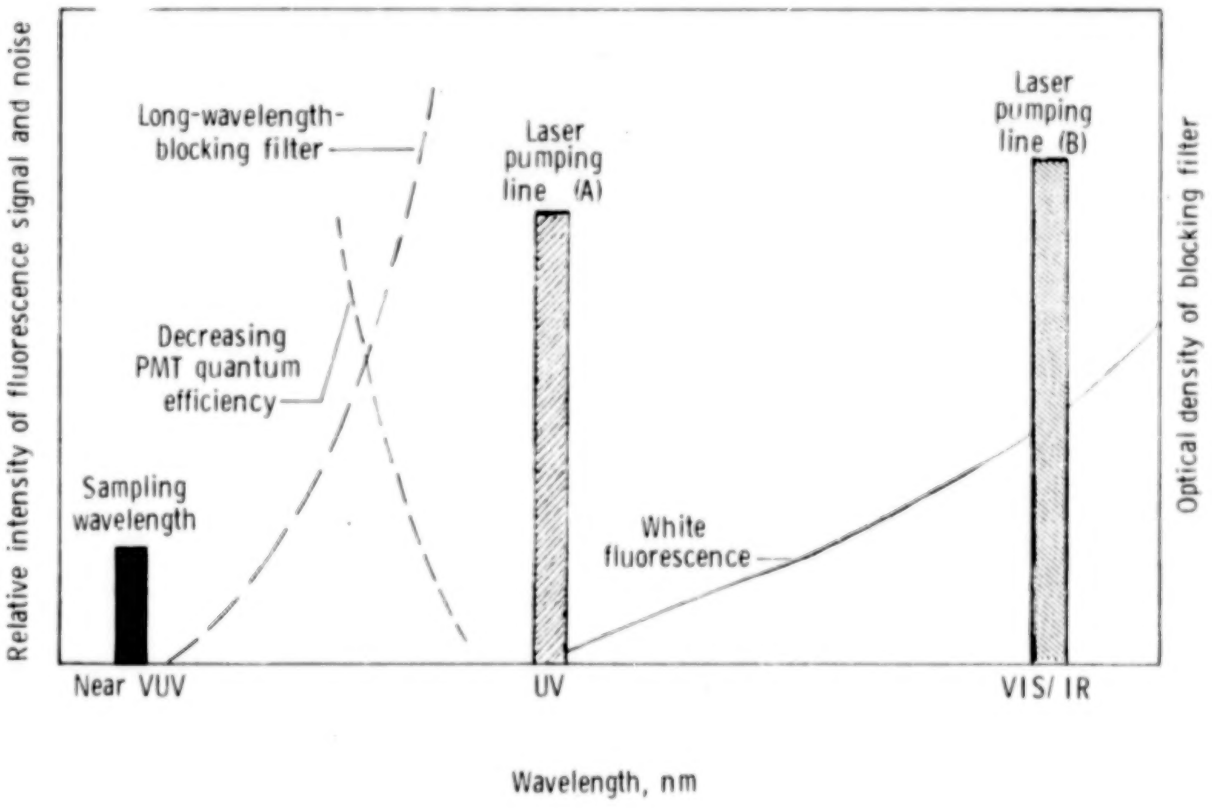

Figure 4.- Two-photon LIF measurement concept.

Figure 5 illustrates the TP-LIF excitation and detection scheme for NO. As in the SP-LIF scheme just discussed, laser pump A at 226 nm is used to excite NO from the $X^2\Pi$ state to the low-lying $A^2\Sigma^+$ state. In the TP-LIF scheme, this first excitation step is followed by a second excitation by laser pump B at 1064 nm to the

$D^2\Sigma^+$ state. In this case, fluorescence occurs in the wavelength range of 187 to 220 nm. Thus, the white fluorescence background noise (generated by the 226- and 1064-nm pump lasers) can be extensively reduced with the use of a long-wavelength-blocking filter and a near-vacuum UV solar-blind PMT. Current laboratory data suggest a 10^4 reduction in white fluorescence background noise can be achieved. As such, the system is signal limited, background fluorescence will typically be less than signal fluorescence, and measurement uncertainty will be defined by the photon statistics associated with the NO signal. With these characteristics, the TP-LIF method will be applicable to NO measurements under high aerosol conditions (in clouds, for example) and in flux measurements using meteorological correlation techniques. Bradshaw and Davis (1982) provide additional details for the TP-LIF technique.

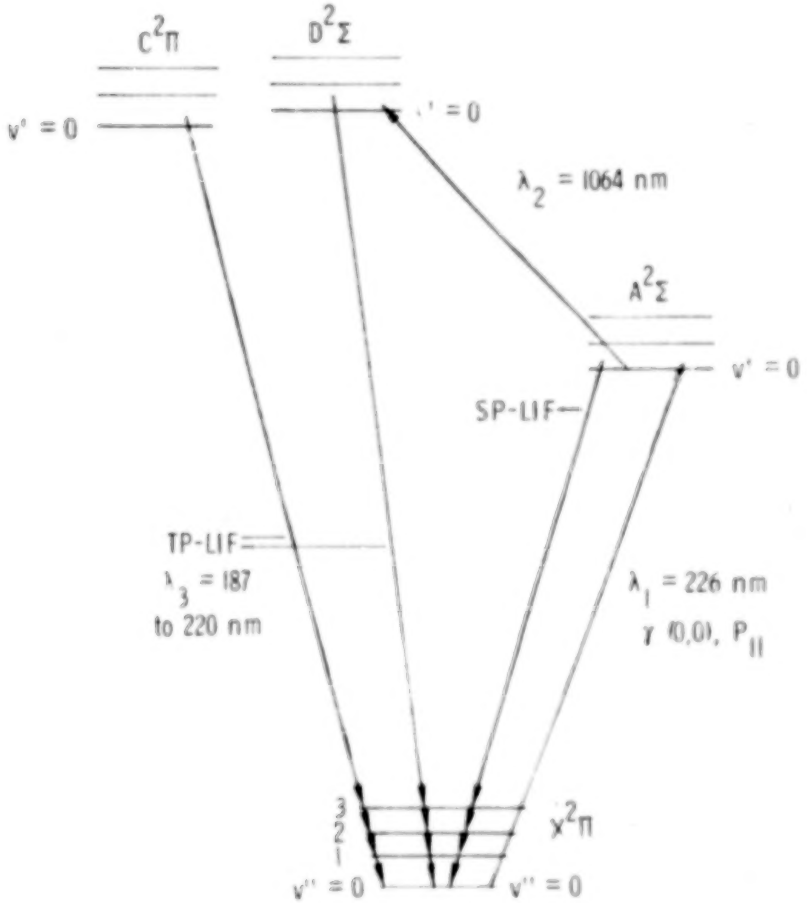

Figure 5.- NO energy diagram for two-photon LIF.

Photofragmentation Laser-Induced Fluorescence (PF-LIF).- The photofragmentation LIF technique is potentially one of the most powerful LIF techniques available for atmospheric chemical measurements. The vast majority of atmospheric molecules do not have bound excited states and thus do not lend themselves to detection by either TP-LIF or SP-LIF techniques. In the PF-LIF method, a given polyatomic species is photodissociated with one laser photon, and one of the photofragments is then selectively excited by a second laser photon into a bonding excited state. The ideal mode in which this operation is carried out is illustrated in figure 6. Here the polyatomic

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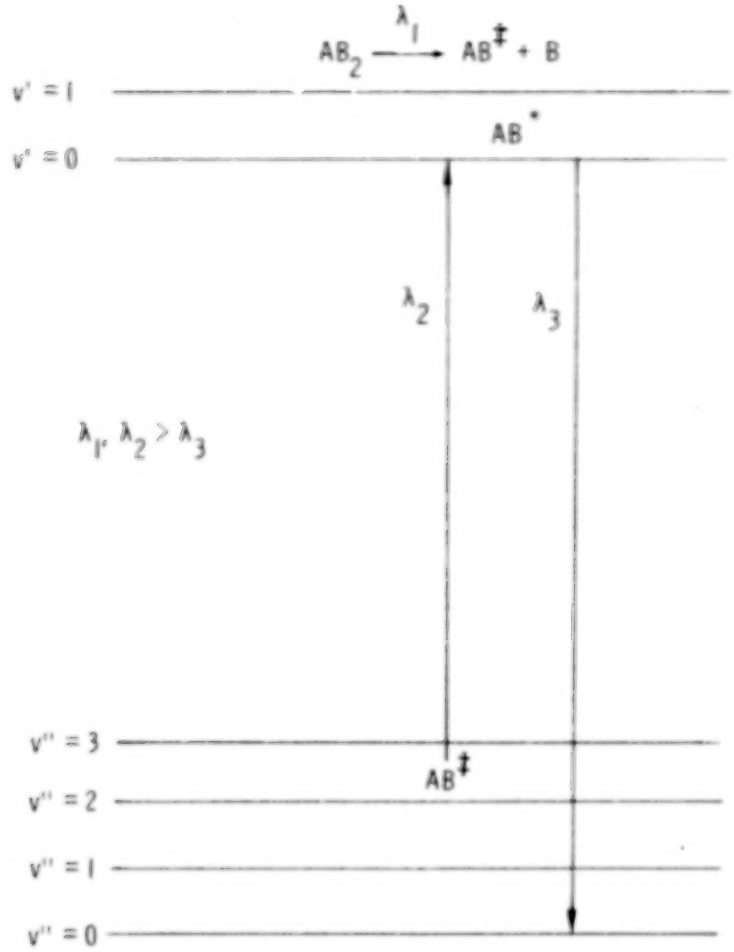

Figure 6.- Photofragmentation LIF measurement concept.

species AB_2 is first photodissociated by laser wavelength λ_1 to form a vibrationally excited photofragment $AB^{\dagger}$. The vibrationally excited photofragment is then excited by a laser wavelength λ_2 into the lowest vibrational manifold of its lowest lying excited electronic state, AB*. Fluorescence from AB* can then occur at several wavelengths, some of which are blue shifted relative to the photofragmentation and fluorescence exciting wavelengths (i.e., $\lambda_3 < \lambda_1$ and λ_2). In the case of the NO_2 molecule, although it does have a bound excited state, its radiative lifetime is sufficiently long to reduce the fluorescence efficiency to a very low value under atmospheric conditions. Figure 7 illustrates a specific PF-LIF excitation scheme for NO_2. It has been established that the preferred photofragmentation wavelength is 308 nm. At this wavelength the excited photofragment from NO_2 is NO. It is formed in excited vibrational levels 1, 2, and 3, and thus several possible excitation schemes for eventual detection exist. Laboratory studies have shown that the preferred sampling scheme involves pumping the v" = 3 level of the vibrationally excited ground state NO into the v' = 0 level of the $A^2\Sigma^+$ state. Thus, fluorescence can be sampled at wavelengths as low as 226 nm, as shown in figure 7. Rejection of white background fluorescence can again be achieved (as for TP-LIF) with the use of long-wavelength-blocking filters in conjunction with solar-blind PMT's. Current studies have shown that operating both laser systems for λ_1 = 308 nm and λ_2 = 259 nm at 10 Hz results in a detected noise level of less than two photons for a 1-hour integration time (i.e., 36,000 laser shots). This is approximately 10^5 times lower in background fluorescence than is expected from a SP-LIF system operating at 226 nm.

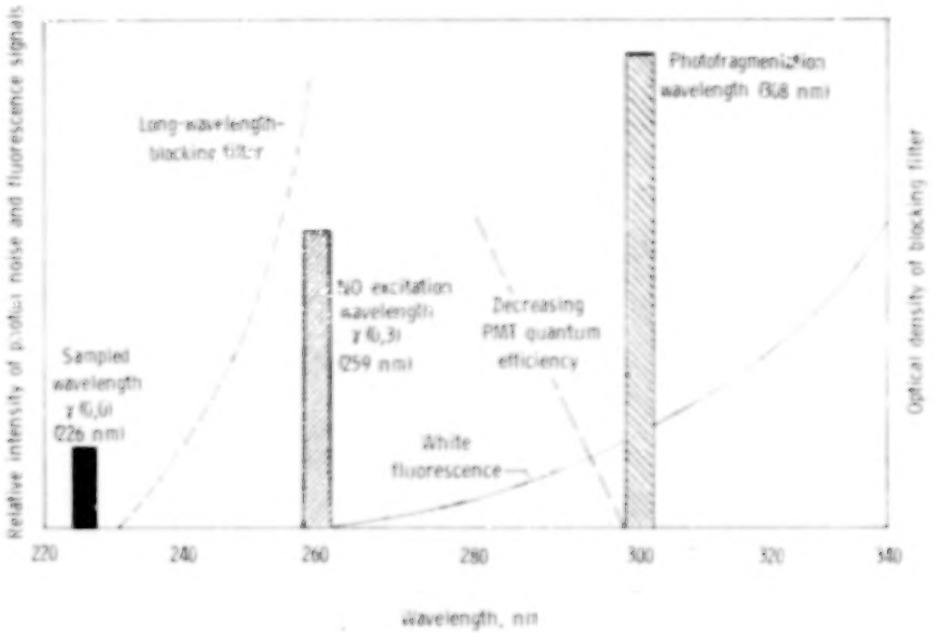

Figure 7.- Photofragmentation LIF NO_2 measurement scheme.

Other N_xO_y species that have been examined in terms of detection by the PF-LIF technique are NO_3 and HNO_2. The detection schemes are similar to those previously discussed. The appropriate photofragmentation and excitation wavelengths are given in figure 8. Further discussion of the PF-LIF technique for detection of NO_2, NO_3, and HNO_2 can be found in Rodgers et al. (1980).

PF-LIF DETECTION OF NO_3

$$NO_3 + h\nu_1 \xrightarrow{\lambda_1 = 589\ nm} NO(X^2\Pi, v'' = 2) + O_2(^1\Delta)$$

$$NO(v'' = 2) + h\nu_2 \xrightarrow{\lambda_2 = 248\ nm} NO^*(v' = 0)$$

$$NO^*(v' = 0) \xrightarrow{\lambda_3 = 226\ nm} NO(v'' = 0) + h\nu_3$$

$$NO_2 \text{ or } HNO_3 + h\nu_1 \not\rightarrow NO(X^2\Pi, v'' = 2)$$

PF-LIF DETECTION OF HNO_2

$$HNO_2 + h\nu_1 \xrightarrow{\lambda_1 = 355\ nm} NO(X^2\Pi, v'' = 3) + O_2$$

$$NO(v'' = 3) + h\nu_2 \xrightarrow{\lambda_2 = 259\ nm} NO^*(v' = 0)$$

$$NO^*(v' = 0) \xrightarrow{\lambda_3 = 226\ nm} NO(v'' = 0) + h\nu_3$$

Figure 8.- Photofragmentation LIF NO_3 and HNO_2 measurement schemes.

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Lidar Laser-Induced Fluorescence (Lidar-LIF).- The lidar-LIF concept employs the SP-LIF excitation scheme in a remote-sensing configuration for detection of various species. The advantages of lidar-induced fluorescence systems are that they permit the efficient use of the available laser power via excitation of a larger volume than can be realized by an in situ LIF system, and the measurement volume is free from contamination by the instrument platform. The principal disadvantage of lidar is its susceptibility to interference from scattered solar flux. Lidar system components include a laser source, transmitting optics, a receiver telescope, a spectral selection and detection system, and signal-processing electronics. Generally, the spectral selection and detection system is specific to the species being detected, and the other components can be used in the detection of other species. The lidar-LIF as used for NO detection is briefly summarized in the following text.

Figure 9 illustrates the specific lidar-LIF pumping and detection scheme used for NO. As was the case for the in situ LIF-SP NO technique, NO is excited using 226 nm radiation at the (0,0) band of the $\gamma(A^2\Sigma^+ \rightarrow X^2\Pi)$ system. Once excited to the $A^2\Sigma^+$ state, NO fluorescence occurs to many vibrational levels of the $X^2\Pi$ state (see figure 9). N_2 Raman scattering at 238 nm and 247 nm makes use of the 237-nm line impossible and the 248-nm line difficult. However, the line at 260 nm is sufficiently removed from the N_2 Raman line that filters (dielectric and/or chemical) provide sufficient isolation for detection.

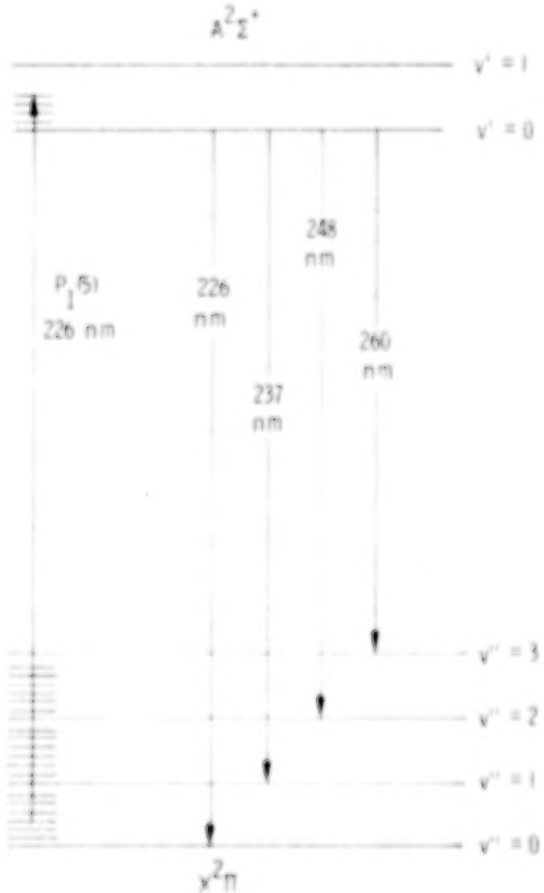

Figure 9.- Lidar-LIF energy diagram for NO detection.

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The current status of the lidar-LIF NO instrument is that a prototype instrument is being tested in the field (aircraft flights). These flights will provide engineering data from which instrument improvements can be made. The system as currently configured is about 4.5 m long and 2 m high at the telescope and weighs about 1300 kg. As the need develops, the system can be scaled down significantly. The distinguishing aspect of this system as compared to other lidars is the techniques used to reduce sky background (that is, pointing upward and using an adjustable polarizer). Looking upward as opposed to horizontally reduces background because less atmosphere is present to scatter light toward the receiver. The polarizer takes advantage of the fact that Rayleigh-scattered light (the source of the background) is strongly polarized, whereas fluorescence from NO is not. Insertion of a polarizer therefore decreases the collection efficiency for the fluorescence by a factor of 2 while achieving a much greater reduction in the background.

The interference effect of most concern is fluorescence from aerosols and other molecules (particularly SO_2) excited by the laser. Scattered solar flux does not present a problem at 259 nm because with proper filtering the background count rate, in principle, can be made negligible. Also, laser production mechanisms for NO should not be significant. Current field testing of the technique should quantify the magnitude of these interferences. Fluorescence branching ratios for the γ band have been measured, as have quenching coefficients. Although strong atmospheric attenuation of both transmit and receive wavelengths occurs due to scattering and ozone absorption, fast and high-quality tropospheric NO measurements are still possible.

Ionization Spectroscopy

Ionization spectroscopy is a comparatively new and sensitive in situ laser technique currently under laboratory investigation for tropospheric NO measurements and is being considered conceptually for NO_2 measurements. The general concept of ionization spectroscopy is well established, having been exploited in spectroscopic studies (Johnson and Otis, 1981; Hurst et al., 1977; Brophy and Rettner, 1979; Smith et al., 1982); however, little data are available pertaining to quantitative determination of trace tropospheric species. The basic concept utilizes one or more pulsed visible or UV laser wavelengths focused between two biased ion collection plates housed inside a sample cell. If the net photon energy absorbed per molecule exceeds its ionization potential, ions will be produced. These ions are collected by the biased plates, amplified by an electrometer, and processed on a single-shot basis by a gated integrator. The resultant processed signal is a measure of the number of molecules of interest in the sample cell. As most molecular ionization potential falls in the range of 8 to 13 eV, three or four visible photons or two ultraviolet photons are generally required for ionization of the molecule.

Ionization spectroscopy can be implemented via two different approaches, namely Multiphoton Ionization (MPI) and Resonant Ionization Spectroscopy (RIS). The MPI approach tends to utilize high-power pulsed lasers which provide the capability of ionizing directly from the ground state of the molecule. This approach can be satisfactorily applied in mixtures of well-defined gases. However, in a complex mixture, such as an atmospheric sample, the MPI approach can ionize a number of different molecules in the sample, thereby producing an unwanted background signal.

An important consideration for ionization spectroscopy, where only total ion current is measured, is the lack of mass resolution (e.g., inability to quantify background interference), and the MPI approach tends to exaggerate this problem. The RIS approach takes advantage of the fact that each species possesses a unique spectroscopic signature which, with a priori knowledge, can be exploited to control

ionization rates. This would then provide species selectivity while minimizing background ionization for the other components. Because of this potential for minimizing interfering effects, the RIS approach is clearly more desirable. For NO, a pure RIS methodology can be considered; for NO_2, the methodology must be classified as MPI, although, as will be seen below, the final step in the NO_2 scheme is in fact RIS.

RIS utilizes two or more laser wavelengths. The first laser is tuned to resonantly excite a specific molecule from its ground electronic state to an intermediate electronic state; this is similar to the process employed in the laser-induced fluorescence (LIF) methods. Before this excited level can be strongly quenched or radiated, it is pumped by another laser which is capable of ionizing only the excited molecules produced by the first laser but is not capable of ionizing the molecule from its ground state. Laser quantum energies are chosen such that the sum of the two laser quanta exceeds the ionization potential of the ground state of the molecule. The net result of the absorption of two or more laser photons is the selective conversion of a specific molecule in a mixture to an ion, which is collected with high efficiency by ion collection optics.

The RIS approach for NO detection is illustrated on the potential-energy curves for the electronic states of NO and NO^+ shown in figure 10. The ionization potential for NO is 9.26 eV and the sum of the two laser quanta must be equal to or greater than this. The three possible RIS detection schemes illustrated in the figure are listed here.

Scheme 1

$$NO(X^2\Pi,\ v'' = 0) + h\nu \xrightarrow{\lambda_1 = 226\ nm} NO^*(A^2\Sigma^+,\ v' = 0) \tag{1}$$

$$NO^*(A^2\Sigma^+,\ v' = 0) + h\nu \xrightarrow{\lambda_2 = 226\ nm} NO^+ + e^- \tag{2}$$

Scheme 2

$$NO(X^2\Pi,\ v'' = 0) + h\nu \xrightarrow{\lambda_1 = 226\ nm} NO^*(A^2\Sigma^+,\ v' = 0) \tag{3}$$

$$NO^*(A^2\Sigma^+,\ v' = 0) + h\nu \xrightarrow{\lambda_2 < 308\ nm} NO^+ + e^- \tag{4}$$

Scheme 3

$$NO(X^2\Pi,\ v'' = 0) + h\nu \xrightarrow{\lambda_1 = 226\ nm} NO^*(A^2\Sigma^+,\ v' = 0) \tag{5}$$

$$NO^*(A^2\Sigma^+,\ v' = 0) + h\nu \xrightarrow{\lambda_2 = 600\ nm} NO^*(E^2\Sigma^+,\ v'\ J') \tag{6}$$

$$NO^*(E^2\Sigma^+,\ v'\ J') + h\nu \xrightarrow{\lambda_3 = 600\ nm} NO^+ + e^- \tag{7}$$

As shown above, the initial step for each scheme is resonant excitation of the ground state of NO at 226 nm on the $\gamma(0,0)$ band to the $NO^*(A^2\Sigma^+,\ v' = 0)$ electronically excited state. For high laser fluxes ($I > 10^{25}$ photon/cm^2 sec) at $\lambda = 226$ nm,

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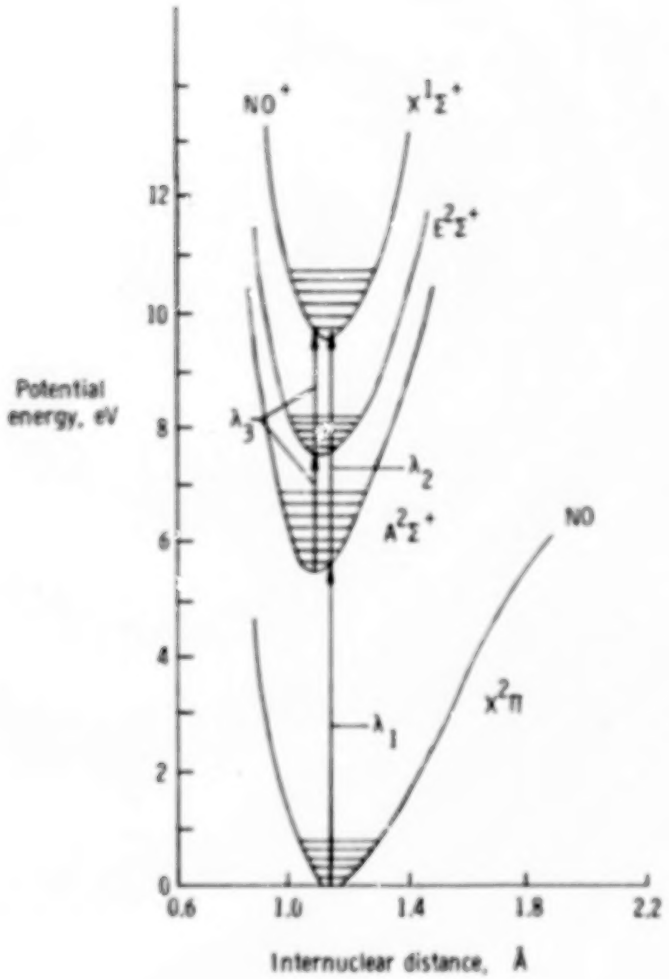

Figure 10.- NO energy diagram for Resonant Ionization Spectroscopy Detection.

a second photon at λ with energy $h\nu_1$ has a large probability of being absorbed by the excited NO, leading to ionization. In this scheme, the total photon energy is approximately 11 eV, and this energy may cause nonresonant ionization of other molecules with ionization potentials less than 11 eV. If this background ionization is negligible for the particular application, then the first scheme offers an advantage of requiring only a single laser source.

The second RIS scheme utilizes a less intense laser source at 226 nm to minimize nonresonant ionization and a second laser at $\lambda < 308$ nm to produce ionization. This second laser can have a larger photon flux because two quanta of photon energy at 308 nm have only approximately 7.5 eV of energy, which is too low to ionize most molecules. If background nonresonant ionization is still too high, the third scheme can be employed. In this scheme, one photon at 226 nm and two photons at 600 nm produce ionization and should eliminate most nonresonant background. Any remaining nonresonant ionization can be measured by tuning the first laser off NO resonance. When the laser is off resonance, any ion signal is due to background, which is subtracted from the ion signal when the laser is on the NO resonance line at 226 nm. The pressure-broadened Doppler linewidth for NO absorption on the $\gamma(0,0)$ band is very narrow (<0.05 Å), and as such, any nonresonant ionization process should not be affected by the small wavelength change.

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By considering the kinetic rate equations, absorption and ionization cross sections, radiative lifetimes, and quenching rates for the various schemes, estimates of the fraction of ground state NO($X^2\Pi$, $v'' = 0$) ionized to NO^+ can be made. Table III summarizes these calculations for a range of laser fluxes and for a sample at 1 atm pressure. As indicated in the table and as allowed by the level of nonresonant background ionization, substantial increases in the fraction of NO ionized are gained by operation at higher photon flux levels. In addition, operation at lower pressures also improves overall NO ionization efficiency. For example, for scheme 2 at 10^{24} (226 nm) and 10^{26} (308 nm) photon fluxes, the NO^+/NO ratio at 0.1 atm is 0.13 compared to 0.04 at 1 atm pressure.

Table III - Fraction of Ground State NO Ionized per Laser Pulse at 1 Atmosphere Pressure

RIS scheme	Laser flux rate, photon/cm^2-sec			NO^+/NO
	λ = 226 nm	λ < 308 nm	λ = 600 nm	
Single laser, 226 nm (scheme 1)	10^{24}	-	-	5.2×10^{-4}
	10^{25}	-	-	2.5×10^{-2}
	10^{26}	-	-	0.44
Two lasers, 226 and 308 nm (scheme 2)	10^{24}	10^{24}	-	8.6×10^{-4}
	10^{24}	10^{26}	-	4.0×10^{-2}
	10^{25}	10^{25}	-	0.11
	10^{25}	10^{26}	-	0.23
	10^{26}	10^{26}	-	0.91
	19^{26}	10^{27}	-	0.99
Two lasers, 226 and 600 nm (scheme 3)	10^{25}	-	10^{25}	2.8×10^{-2}
	10^{27}	-	10^{27}	0.99

An energy diagram illustrating the electronic states of NO_2 which are applicable to ionization spectroscopy detection principles is shown in figure 11. Ionization of NO_2 is controlled by fast predissociations (Morrison et al., 1981) leading to NO + O. The lifetime of the ^2B state is so short that no NO_2 survives to be ionized and detected as NO_2^+. Instead, the detection of NO_2 is based on RIS detection of the NO fragments produced by laser excitation of the NO_2 molecule, such as

$$NO_2 + 2h\nu \longrightarrow NO_2^* + NO(X^2\Pi_i, v'', J'') + O(^1D) \quad (8)$$

$$NO(X^2\Pi_i, v'', J'') \xrightarrow{nh\nu} NO^+ + e^- \quad (9)$$

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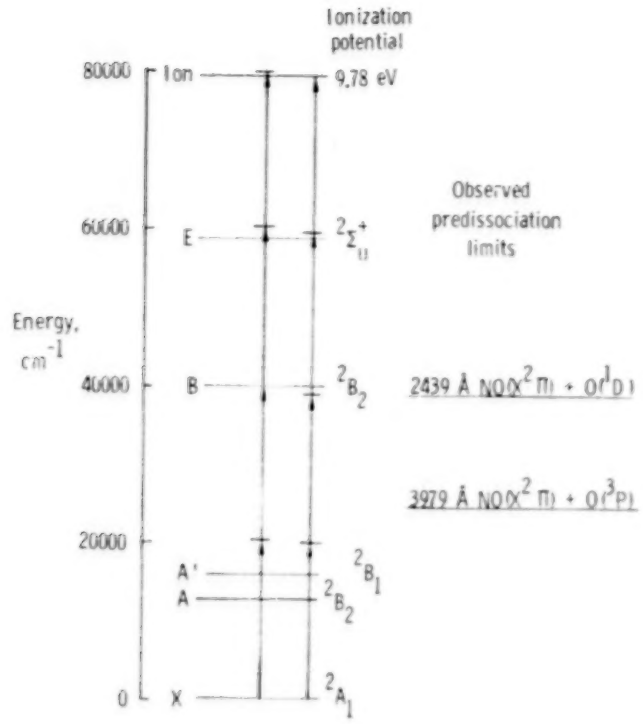

Figure 11.- NO_2 energy diagram for multiphoton ionization detection.

Because of the dissociation of NO_2, the ionization spectroscopy scheme described here is, in the strictest form, an MPI approach. The existence of these NO fragments is further illustrated by the data of figure 12. The top half is an ionization spectrum of NO_2 with a quadrupole mass spectrometer tuned to detect only the ions produced at mass 30 (NO^+). The additional features present in the lower spectrum are attributed to the above NO fragments and thus provide a means for detection of NO_2. For all laser wavelengths investigated below 455 nm, the branching ratio defined by NO^+ to NO_2^+ is at least 500 to 1.

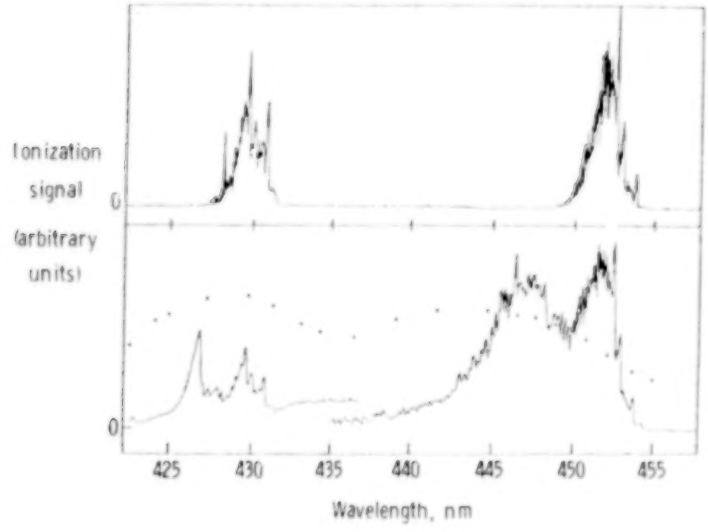

Figure 12.- Multiphoton ionization spectrum for NO_2 detection.

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Although the above detection schemes for RIS and MPI are conceptually sound for detection of mixtures containing NO or NO_2, modifications may be necessary when dealing with mixtures containing both NO and NO_2. The photodissociation of NO_2 is a source of production of some NO in the $X^2\Pi$, v" = 0 state, and thus may become an interference for any NO measurement if proper care is not taken in the experiment. To solve this problem for MPI, it is suggested that NO_2 be detected using MPI at 283 nm. What is measured in this case is the ionization spectrum resulting from NO fragments generated in the v" = 5 state. There is no contribution to the ionization signal at this wavelength from NO in the initial air sample. The NO_2 concentration can in principle be quantitatively established by calibration with NO_2 standards, thus eliminating the need to determine photolysis efficiency into NO (v" = 5) state. NO concentration in the air sample is determined by the previously discussed RIS scheme at λ_1 = 226 nm and $\lambda_2 \leq$ 308 nm. However, in this case a total NO measurement is made which includes the NO initially in the sample plus NO fragments from any NO_2 photodissociation into the v" = 0 state. Calibration with known standards can provide the instrument sensitivities required for quantitative determination of NO.

It is anticipated that development of such a laser ionization scheme to operational status will result in an instrument capable of measuring NO and NO_2 at global tropospheric concentration levels. Sources of interference from other NO_x compounds that may be present in a tropospheric air sample need to be investigated, but these are limited to compounds that may produce signals at wavelengths used for the RIS method.

Absorption Spectroscopy

The terminology "absorption spectroscopy" is used here to encompass a general class of techniques that measure a change in the radiance from some source due to absorption occurring as the radiance is directed over a known path length. This measurement approach is, in general, very versatile as well as being species specific. As considered here, this technology includes techniques that utilize broadband or monochromatic laser sources and employ the UV to IR spectral region. Detection and quantitation of the concentration of a given trace gas via absorption spectroscopy are based on the existence of a unique spectral signature associated with the gas as well as on the capability to isolate an absorption line or feature which is free from interference from other atmospheric compounds. Ironically, both the simplicity and the complexity of this technique stem from the fact that the unique spectral features exhibited by the target gas are quite often intermingled with the spectral signatures exhibited by most trace atmospheric gases.

The IR spectral region has traditionally been considered the "fingerprint" of the atmosphere because most polyatomic molecules have vibrational-rotational bands in the IR. However, the UV and near-UV spectral region is of particular interest here because a number of N_xO_y species exhibit well-defined spectral features in this region. The two measurement methodologies generally used in both the UV and IR regions can be characterized as either general survey or species specific. The survey approach is typified by atmospheric absorption spectra obtained over wide continuous spectral regions, whereas the species-specific approach is generally restricted to a very narrow spectral region around an isolated absorption line associated with the desired molecule. The advantage of the survey approach is the large information content, which can often be used to identify and correct for interfering constituents. The disadvantage is the complexity associated with large data rates and data interpretation. The advantage of the species-specific approach is the lower data rates, and data interpretation is generally straightforward, lending itself to real-time results. The disadvantage is the susceptibility to unknown interfering affects.

The workshop reviewed two survey type techniques and one species-specific technique. The survey approaches were Fourier Transform Infrared Spectroscopy (FTIR) and Long-Path Absorption. The species-specific approach was Infrared Tunable-Diode Laser Spectroscopy. A brief discussion of the salient features and potential of each approach is given below.

Fourier Transform Infrared Spectroscopy (FTIR).- Fourier transform spectroscopy is one of the more conventional techniques in absorption spectroscopy and can be used in either a remote or an in situ configuration (Mankin, 1979). In application, the Fourier transform of a portion of the transmission spectrum of the atmosphere is recorded and absorption patterns or features known to be associated with the molecule are identified. Each molecule generally has unique absorption signatures that provide an unambiguous identification of the molecule's presence. Quantitative determination of the concentration present is somewhat more problematic due to overlapping spectra from other absorbing molecules in the air sample. When used as a remote sensor, the Sun generally serves as a thermal source, with the optical depth of the measurement in effect limited by the ambient distribution of the species of interest. In this mode, FTIR has found extensive applications in remote sensing of the stratosphere from both ground and balloon platforms. In the in situ mode, a thermal source is used in conjunction with a multipass (sample cell) absorption cell.

FTIR detection with a long-path cell has been used in both ground-based and airborne systems. A cell of 1 km path length has been used on the ground and a cell with a path length of 160 m has been flown. The sensitivity of the technique is determined by the achievable path length and the minimum detectable absorption. Because of difficulties in defining the baseline signal level, absorption less than 1 percent cannot reliably be measured. This places some limitations on the lowest attainable detection limit. The detection limit volume mixing ratio, μ_{min}, can be calculated from Mankin (1980):

$$\mu_{min} = \frac{K_{min}\,\pi\alpha_o}{SL} \tag{10}$$

where S line intensity, $cm^{-1}/cm\text{-}atm$

L path length, cm

α_o pressure-broadened line width, cm^{-1}/atm

K_{min} minimal detectable absorption

For a species with a strong absorption line ($S \approx 10$, $\alpha_o \approx 0.08$), detection limits of approximately 2.5 and 15 ppbv can be obtained with path lengths of 1 km and 160 m, respectively, assuming minimal detection of about 1 percent absorption ($K_{min} = 0.01$).

FTIR has been applied to the detection of HNO_3 and PAN. Using a ground-based system with a 1-km cell, detection limits of 6 ppbv (HNO_3) and 3 ppbv (PAN) have been observed. Although an airborne system has not been developed for N_xO_y compounds, CO measurements with the airborne 160-m cell show detection limits of approximately 15 ppbv at 1 km altitude. While FTIR can be used for tropospheric measurements of HNO_3 and PAN, it is unlikely to have sufficient sensitivity for measurements in the free (clean) troposphere.

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Infrared Tunable-Diode Laser Spectroscopy.- This is a technique which in general is very versatile as well as being highly species specific. In this approach, a monochromatic source, such as a tunable-diode laser, is scanned over a narrow wavelength region around a particular absorption line or feature of the gas of interest. The high sensitivity of the tunable-diode laser concept is attributed to two factors. First, the spectral radiance of the diodes is 10^8 to 10^{12} higher than that of thermal sources, which means that most measurements are not limited by detector noise and more reflections in a White cell may be used to increase the optical path length before losses are unacceptable. Second, and perhaps more important, is the rapid tunability of the laser. With rapid scanning back and forth across an absorption line, the absorption signals appear as an a.c. signal at twice the tuning frequency and can be sensitively detected by synchronous demodulation. Measurement of absorption to approximately 1 part in 10^5 has been demonstrated.

The versatility of the tunable-laser spectroscopy approach stems from the fact that the basic system design can be used for any molecule for which an overlap between an absorption feature and laser emission can be found, as well as the fact that semiconductor diode lasers are available from commercial sources from approximately 3 to 30 μm. Tunable-diode laser systems currently exist for CO (Hinkley et al., 1976; Sachse et al., 1977; Miller et al., 1980) and have been developed in the laboratory for N_xO_y compounds (Cassidy and Reid, 1982) and in particular for NO, NO_2, and HNO_3.

The basic components of a typical system are illustrated in figure 13. The cryogenically cooled laser is tuned to the frequency of the particular absorption feature of interest, and this center frequency can be modulated via the injection current at rates up to 10 kHz. In practice, the typical scanning rate ranges from 1 to 2 kHz. A small percentage of the TDL power is diverted along an optical leg that contains a gas reference cell along with a detector and electronics to lock the TDL frequency sweep on or near the center of the absorption line of interest. TDL power transmitted by the first beam splitter is mechanically chopped at a frequency less than the TDL current modulation and then split into two optical paths. Automatic gain control circuitry processes the chopped TDL signal to normalize the instrument output with respect to drifts in the detectors and electronics and to

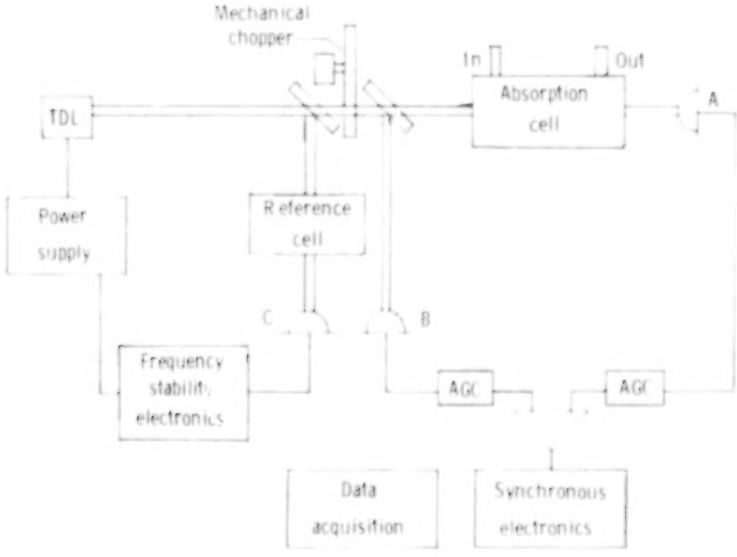

Figure 13.- Basic detector for tunable-diode laser technique.

electronically balance the output signals from the A and B detectors (shown in figure 13). The B detector serves as a common mode rejector of undesired signals on the laser beam. For example, the TDL current sweep generates amplitude modulation in addition to frequency modulation. If uncorrected, the second harmonic of this amplitude modulation would generate a bias offset at the instrument output. The use of the B detector can provide real-time removal of this baseline shift. The output of the A-B differential amplifier is simply the absorption signal interrupted at the mechanical chopper rate. Synchronous electronics detect the absorption signal at the second harmonic of the laser modulation frequency, and the instrument output is recorded on a small desktop computer. The measurement path, along optical leg A, is typically a low-pressure multipass optical cell, although some application may, in fact, require direct measurement in the atmosphere. The reference and sample cells are operated at the same pressure, typically 50 torr. An important consequence of maintaining the measurement path at 50 torr is that at reduced pressures the absorption lines are narrower, thereby reducing the range over which the laser must be tuned and consequently the possibility of interference by a nearby absorption line of another species.

In addition to the above FM modulation detection scheme, the laser can be used simply as a monochromatic source. In this mode, the sensitivity is two orders of magnitude less than the FM scheme above; however, by adding a large number of rapid scans and employing analog cancellation of the laser power variation, sensitivities approaching the FM detection scheme can be achieved. This approach is called sweep integration. The sweep integration scheme can be useful for detecting the presence of interferences, whereas the FM scheme provides continuous specific data over a very narrow spectral region. In practice, both techniques will probably be used.

The two dominant noise sources in the tunable-diode laser systems are noise uniquely associated with the semiconductor laser itself and an optical noise associated with spurious etalon effects in the multipass cell. The laser-related noise appears to be peculiar to semiconductor lasers and in fact appears laser dependent. Various aspects of this noise have also been documented for other applications (e.g., communications). The optical noise is, to some degree, dependent on the laser noise as well as on the design and quality of the optics. The design and quality of the multipass cell as well as the characteristics of the laser output affect the maximum path length that can be obtained and consequently the overall system sensitivity. Various approaches have been used to optimize system sensitivity with respect to laser and optical noise and have demonstrated sensitivities of 1 part in 10^5. With improvements in semiconductor lasers, higher sensitivities should be achievable.

Assuming system sensitivities sufficient to measure signal changes of 10^{-5}, a detection limit of approximately 3 pptv for a 1-km path length can be expected for most species. For NO, which has lower absorption line intensities than most species (by a factor of 2), and considering a reasonable path length (folded) of 300 m for an airborne application, the detection limit should occur at about a 20 pptv level.

Calibration of the tunable-diode laser for NO requires that the reference cell NO concentration be known and stable. Standard NO in N_2 mixtures used for calibration of conventional NO in situ instruments and as the reference cell concentration are typically 1 ppmv.

Detection limits for NO_2 (airborne unit, 300-m path length) can be expected to be about 10 pptv because NO_2 absorption line intensities are higher than NO and tend to be more typical of polyatomic molecules in general. NO_2 sensitivities of 75 pptv for a 40-m path length have been demonstrated. Calibration of the tunable-diode

laser system for NO_2 is more problematic than for NO since accepted NO_2 calibration standards use permeation tubes and NO_2 concentrations are less stable in the reference cell.

Detection limits of the tunable-diode laser system for HNO_3 are expected to be similar to that for NO_2 (i.e., ≈10 pptv). Currently, acceptable HNO_3 calibration standards are difficult to prepare, and therefore a reference cell containing known HNO_3 concentrations is a potential problem.

Long-Path Absorption.- The long-path absorption method is a remote sensing technique which is typically operated over open terrain with optical paths as long as 10 km. As with the other absorption spectroscopy techniques discussed here, detection and quantitation for a species are based on identifying well-known features in the absorption spectrum of the species. The technique is applicable to the detection of various atmospheric gases having UV absorption spectra, including NO, NO_2, NO_3, and HNO_2 (Platt et al., 1979, 1980a, b). The application of the technique is nearly identical for each species, differing only in the areas of optical path length and the location of the absorption feature of interest in the absorption spectrum of the species. The spectral positions of these absorption bands or features for NO, NO_2, NO_3, and HNO_2 are shown in Table IV. In the case of NO_3, the absorption bands are located in the visible part of the spectrum, for NO_2 and HNO_2 they are in the near UV, and for NO in the far UV. In some cases, absorption by other atmospheric compounds may limit the optical path length over which the measurement can be made; for example, absorption by O_3 and O_2 limits the optical path to about 1 km for the NO measurement.

Table IV - Long-Path Absorption Parameters for N_xO_y Species

Species	Position of bands (approx), nm	Differential absorption cross section[a], cm^2	Detection limit, 10-km light path, ppbv
NO	225	1.5×10^{-18}	0.1[b]
NO_2	320-450	1.1×10^{-19}	0.1
NO_3	625, 662	1.5×10^{-17}	10^{-3}
HNO_2	320-390	4.8×10^{-19}	0.02

[a]Absorbance measured with a spectral resolution of approximately 0.7 nm.
[b]1-km path length.

This measurement concept is similar to that for the diode laser spectroscopy, with the major differences being the light source and the measurement path. As it is currently employed, the measurement system consists of a Xe lamp at the focal point of a spherical mirror which directs the light source through the atmosphere to a plane mirror at a distance of a few kilometers. The source radiaton is returned along the outgoing path to a detection system located close to the light source.

The detection system consists of a spherical mirror which focuses the incoming light on the entrance slit of a double monochromator with relatively low spectral

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resolution (0.7 nm). The exit slit is wide, cutting out a 20- to 30-nm-wide portion of the spectrum. This spectral band is scanned rapidly by a narrow slit placed radially around the periphery of a rotating disc. The transmitted light is observed by a photomultiplier. Subsequent scans are added up by a microprocessor, which also provides housekeeping and data handling. Spectral positions are checked by use of a reference gas cell.

In most cases, the measurement signal is a superposition of the signature of several trace gases and has to be unfolded to obtain the absorption information for the species being measured. This is illustrated in figure 14. Trace (a) is the absorption spectrum of air for simultaneous measurement of O_3, NO_2, and CH_2O. This measurement was made along a 6-km path length at a North Sea site in 1978 (Platt et al., 1979). The dominant feature of trace (a) is caused by the absorption spectrum of O_3 as verified by comparison with a spectrum from pure O_3 in air obtained from a calibration gas cell placed before the entrance slit of the monochromator (trace b). The numerical comparison of the two spectra allows one to deduce that the average O_3 concentration along the light path is 31 ppbv. Subtracting the O_3 reference spectrum normalized to 31 ppbv from the original air spectrum yields trace (a - b). It is dominated by features due to NO_2 absorption, also shown as trace (d), which was obtained by placing a reference cell containing pure NO_2 in air in front of the entrance slit of the double monochromator. Comparison yields 2.7 ppbv for the mean NO_2 concentration along the 6.3-km light path. The remaining spectrum represents CH_2O. Demonstrated sensitivities are listed for the N_xO_y species in Table IV.

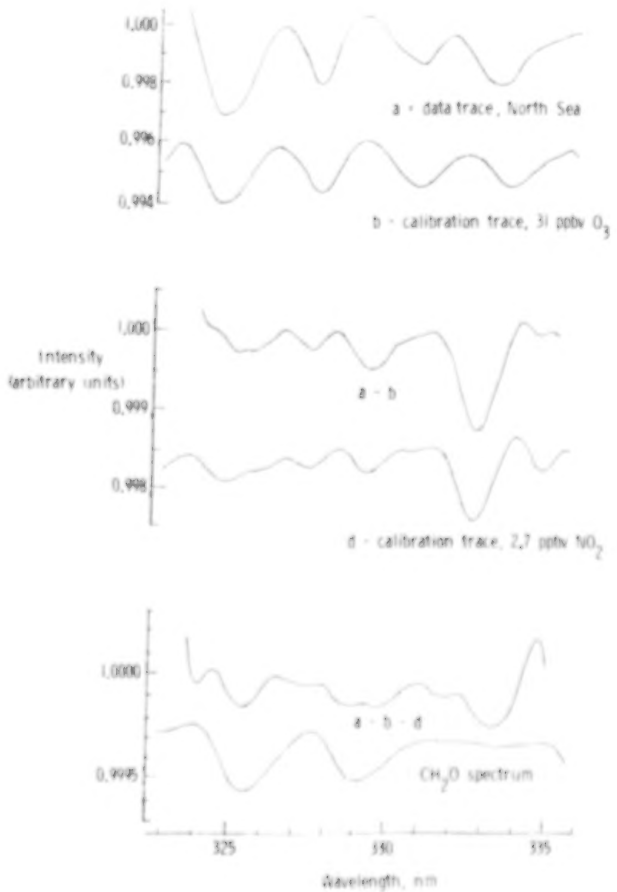

Figure 14.- Data trace illustrating long-path UV absorption technique for NO_2 (Platt et al., 1979).

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Photothermal Spectroscopic Techniques

Numerous laboratory studies have demonstrated the capability of photoacoustic detection, as well as more recent phase fluctuation optical heterodyne sensor (PFLOHS) techniques, to detect molecules of atmospheric interest in the ppbv and sub-ppbv range (Fried and Hodgeson, 1982; Terhune and Anderson, 1977; Koch and Lahmann, 1978; Campillo et al., 1980). These two techniques fall under the broad classification of photothermal spectroscopy and are closely related, but involve different measurement schemes. In both techniques, sensitive detection is accomplished by selectively exciting transitions of the gas of interest with a chopped CW or pulsed laser source. At pressures near atmospheric, collisional de-excitation by the non-absorbing buffer gas rapidly converts the absorbed energy into translational energy. This leads to a modulated local temperature rise and an expansion of the background gas. The resultant pressure change can be detected in photoacoustic studies by a microphone located in the wall of the sample chamber. Alternatively, in PFLOHS detection the change in the local number density can be determined from a concomitant change in the refractive index induced by the density change. In the latter technique, the sample flow is directed across one arm of an ultrasensitive laser heterodyne interferometer in which the excitation laser and a single-frequency He-Ne laser pass collinearly. Small absorptions with coefficients as low as 10^{-10} cm^{-1} can be detected by a change in phase of the reference laser which passes through both arms (Campillo et al., 1980; Davis, 1980).

Photoacoustic Detection.- NO_2 is one of the few atmospheric species that exhibits strong absorption throughout the visible. Because of the quasi-continuous nature of this absorption, photothermal measurements can be carried out using a variety of laser sources. In recent photoacoustic studies (Fried and Hodgeson, 1982; Fried, 1982), a CW argon ion laser was used to excite NO_2 continuously flowing through a nonresonant stainless-steel photoacoustic cell. Photoacoustic signals were detected by an electret microphone and processed by a bandpass filter and lock-in amplifier. Estimates of the system detection limit were obtained by extrapolating the signal-to-noise ratio (S/N) measured in the 250- to 500-ppbv range down to the limit where S/N = 2. The detection limit was consistently found to range from 4 to 10 ppbv. The detection limit of this system is governed by noise associated with rather large background signals arising from three sources: (1) ambient noise at the chopper frequency, (2) scattered laser light impinging on the microphone, and (3) absorption of the laser radiation by the cell walls and windows. Although the background response from these sources is routinely subtracted from the total detector output, the time-dependent variation and the necessity of measuring a small difference between two large signals ultimately limit the detection sensitivity. Obvious solutions such as increasing the laser power to effect a greater NO_2 absorption also increase the background absorption and little improvement is noted.

One means of improving the performance of photoacoustic detectors and at the same time reducing troublesome background signals is to use a resonant photoacoustic cell. In such systems the incident laser radiation is modulated at a natural resonance of the sample chamber. This generates standing acoustic waves, the amplitude of which is enhanced relative to the induced pressure variation generated in a single heating cycle in a nonresonant cell. In addition, since the scattered radiation absorbed at the cell walls only weakly couples to the standing acoustic wave, and acoustic nodes can be placed at the cell windows, background signals can generally be reduced. Such an approach has been investigated in the laboratory (Fried and Stedman, 1979) showing modest improvement to 2 ppbv (S/N = 2). Although only a modest improvement was noted, the detection limit was limited by signal noise (preamplifier and electronics) rather than background noise. To date, the most

sensitive photoacoustic detection limit for NO_2 has been achieved using a higher power argon ion laser coupled to a carefully designed resonant photoacoustic cell (Terhune and Anderson, 1977) and, in a second study, using a discretely tunable IR CO laser coupled to a nonresonant cell (Kreuzer et al., 1972). An extrapolated detection limit of 200 pptv (S/N = 2) has been reported in both cases. In the latter, the sensitivity limiting factor was the noise of the microphone and associated electronics. One of these investigators (C. K. N. Patel, private communication, 1982) anticipates that the 200-pptv detection limit can be reduced down to a few pptv using a 1-W laser, wavelength or Zeeman modulation, a recently improved photoacoustic cell (Patel and Kerl, 1977) and a 100-second integration time constant.

Phase Fluctuation Optical Heterodyne Detection.- Photoacoustic techniques are ultimately limited by the inefficiency of coupling sound, which is generated by the laser-induced absorption, into a microphone transducer. Phase fluctuation optical heterodyne detection is perhaps inherently more sensitive since it eliminates this inefficient step and shows potential for improvement of photothermal detection to the pptv level.

In a preliminary study (H. B. Lin and A. Fried, unpublished results, 1982), the output of an argon ion laser was used to excite calibrated mixtures of NO_2 flowing through one arm of an interferometer. The time-varying refractive index change, induced by the absorption, modulated a He-Ne probe laser passing through both interferometer arms. This modulation was processed by heterodyning with the reference beam on a photodiode. The interferometer was maintained at its optimum linear operating point, halfway between constructive and destructive interference, with a low-frequency servo system. An NO_2 detection limit around 98 ppbv was achieved using this configuration. Significant improvement should be obtained by employing a more stable interferometer configuration and a more effective acoustic enclosure. More importantly, however, the detection limit in this system is governed by the absorption of the excitation laser in the beam splitters used to couple the excitation and probe beams. This effect is equivalent to the window absorption in photoacoustic schemes and is quite significant when visible excitation wavelengths are employed. Excitation in the IR using a CO laser coupled with the system improvements discussed above should therefore effect a significant improvement in detection limit to well below 100 pptv.

Photothermal detection of NO_2 employing visible excitation also suffers from interferences. These include O_3, NO_3, atmospheric aerosols, and possibly overtone absorptions of water vapor. The magnitude of O_3 and NO_3 interferences is dependent upon the spectral region selected for NO_2 absorption, and for the 430- to 450-nm region using a pulsed dye laser it is minimized at about 10 pptv each (based on absorption data and expected species concentrations). Conceptually, the most promising photothermal detection scheme, which minimizes interferences as well as cell wall and window-like absorptions, involves coupling photothermal detection with Zeeman modulation using an IR CO laser (Freund et al., 1976). Further research on this approach will determine its capabilities and limitations.

Collection Techniques

Filter Technique.- As shown in Table II, filter collection is one of several collection techniques considered and is applicable to NO_3^- aerosol and HNO_3 measurements. In fact, most ambient HNO_3 measurements published to date have employed filter collection methods. The technology for filter sampling is simple, straightforward, and reliable. A pump draws air through a series of two filters and a mass flow meter. Aerosols are collected by the first filter, or prefilter (Teflon), and

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HNO_3 vapor is collected by the second filter (nylon). After sampling is completed, the nylon filter is extracted with an aqueous buffer, dissolving its collected HNO_3. Ion chromatographic analysis of the NO_3^- in this extract quantifies the mass of HNO_3, which when divided by the mass of air sampled yields the ambient HNO_3 concentration. Aerosols collected on the prefilter can be analyzed to determine the NO_3^- aerosol ambient concentration.

Only Teflon and acid-washed quartz filters have been used as prefilters; other materials tend to absorb the nitric acid vapor, reducing the amount that reaches the nylon filter. Successful alternatives to nylon mats for collecting the HNO_3 include cellulose filters impregnated with a variety of substances, such as NaCl, carbonates, or organic bases.

Filter sampling has several disadvantages. Sampling times are relatively long, typically 1 hour at flow rates of 5 to 10 scfm for a S/N of 2 at pptv levels. At higher concentrations the sampling time can be shortened accordingly. About 1 hour is required to extract and analyze the filters, and if the ion chromatograph is taken into the field with the sampler, final data can be obtained during a field operation.

Probably the greatest disadvantage of the filter technique for HNO_3 is the potential for positive and negative artifacts. A negative artifact would occur if either the prefilter or aerosols loaded on it were to collect HNO_3 vapor, preventing it from reaching the nylon filter. This is unlikely to be a problem if the Teflon or acidified quartz prefilters are not loaded heavily nor exposed for long periods of time in an aerosol-rich atmosphere. Positive artifacts are generally of greater concern. They may result when incoming H_2SO_4 or SO_2 vapor reacts with NO_3^- aerosols already collected by the prefilter, displacing HNO_3 vapor and leaving an $SO_4^=$ salt behind on the prefilter. This "artifact HNO_3" is then collected by the nylon filter just as if it had been HNO_3 vapor in the atmosphere. A similar artifact can occur if NH_4NO_3 aerosol evaporates from the prefilter, forming both NH_3 and HNO_3 vapors.

The potential NH_4NO_3 artifact is a subject of intense debate. Attempts to measure this artifact necessarily disturb the equilibrium between NH_3, HNO_3, and NH_4NO_3, producing ambiguous results. Depending on the experiment and on test procedures used, results have varied significantly, showing NH_4NO_3 losses from a few percent to over 50 percent (Tang, 1980; Appel et al., 1981; Forrest et al., 1982; Spicer et al., 1982; Shaw et al., 1982). Most experimenters will agree that NH_4NO_3 evaporation can produce a positive artifact during long sampling intervals in polluted atmospheres. But some investigators suggest that NH_4NO_3 will not even exist in clean air (because relatively high ppbv levels of HNO_3 and NH_3 are needed to form it) and that short sampling under relatively homogeneous conditions would prevent its evaporation anyway. Thus, there is currently some uncertainty as to the importance of this artifact in global tropospheric sampling.

Filter methods have substantial advantages. First, they are simple and reliable, with almost no instrument down time. Filters can be broken or contaminated, but generally data recovery is nearly complete. Second, the sensitivity is known to be adequate even for the cleanest parts of the globe, and third, bulk aerosol data are virtually free, being gained by analyzing the prefilter.

The nylon filter method for HNO_3 has been well tested. Field intercomparison tests (in smog conditions) with other methods resulted in the nylon filter data having (at 95-percent confidence level) a slope of 1.02, an intercept of zero, and a correlation coefficient of 0.91 when regressed against median values from several different HNO_3 methods. Other laboratory and field tests show that absolute accuracies of 10 percent can be obtained at precision levels of 1 percent.

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Condensation Technique.- Another collection approach, the condensation technique, is applicable to the measurement of many tropospheric trace gases, including HNO_3 and HNO_2 (Farmer and Dawson, 1982). Application of the technique requires that the gas of interest be highly soluble in water. If a surface is cooled below the dew point of the surrounding air, it does two things: it produces a boundary layer of free convective flow, which is laminar under most conditions, and it collects water vapor. If the surface is sufficiently clean and smooth, the condensate forms a film which drains from the surface and can be analyzed. The rate of collection of condensate and its chemical composition are determined by heat and mass transfer and by the concentrations of trace substances in the sampled air. Under most conditions, particulates are collected inefficiently and therefore make a negligible contribution to observed concentrations. Highest collection efficiency is found for highly soluble gases.

Application of the condensation technique for ambient measurements of HNO_2 and HNO_3 requires about a 1-hour sampling period (determined by film drainage). Sensitivity depends on the condensation rate but is usually limited by the chemical analysis technique, which is ion chromatography. Without preconcentration of the condensate prior to analysis, lower detection limits are about 50 pptv for both HNO_2 and HNO_3. Preconcentration can lower this to about 5 pptv. Accuracy and precision are estimated (based on comparison studies) to be 30 and 9 percent respectively. Current instrument design does not permit rigorous direct calibration. Future design of the instrument will permit not only direct calibration but also additional identification of selectivity and interference parameters.

This method, by its nature, cannot distinguish between substances present in the air and those resulting from aqueous reaction (e.g., hydrolysis). Apart from N_2O_5 (which could be collected as HNO_3 but is expected to be present at very much lower concentrations), HNO_3 determinations should be little affected by hydrolysis. HNO_2, however, will probably have some contribution from PAN, but less than what would be deduced from the relative mixing ratio. The contributions of NO and NO_2 to observed HNO_2 concentrations are expected to be small. However, further work is required to demonstrate this.

Tungstic Acid.- The tungstic-acid technique (TAT) is a relatively new in situ sampling procedure which offers the potential for simultaneous measurements of ambient levels of gaseous and particulate nitric acid. This technique inherently collects NH_3 and HNO_3 simultaneously. Accordingly, the following discussion will cover the analysis procedure for NH_3 and HNO_3. The basic technique has been described by Braman et al. (1982) and field-tested from a ground-based platform by McClenny et al. (1982). Airborne tests of an automated system using the TAT are currently under way at the Langley Research Center. Collection of the gaseous species is similar to the diffusion denuder techniques, whereas the aerosol collection is similar to the filter type techniques. For both species, however, the collection medium is WO_3. Figure 15 illustrates the basic components of the collection system. Ambient air is drawn through a hollow diffusion tube coated on its interior with WO_3 and then through a tube packed with WO_3-coated sand. With laminar flow established, gaseous HNO_3 and NH_3 are absorbed on the WO_3 in the diffusion tube while the aerosols pass through and are collected in the packed tube. Even though the details of the absorption process are not fully understood, laboratory studies by Braman et al. (1982) suggest that it is highly selective with respect to the gaseous phase of NH_3 and HNO_3. Correlative-type studies also support the selective absorption properties of the WO_3 coating for both NH_3 (Harward et al., 1982) and HNO_3 (Shaw et al., 1982).

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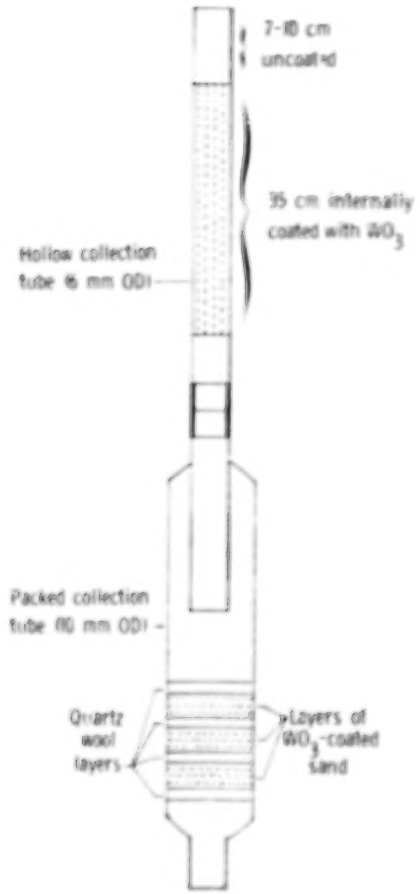

Figure 15.- Hollow and packed tube design for tungstic-acid collection technique.

Sample analysis for each collection tube (hollow and packed) is performed as a two-step process resulting in separation and detection of the NH_3 and HNO_3 components. The analysis technique is based on conversion of each component to NO and ultimate detection via an NO_x chemiluminescence analyzer. Collected samples are thermally desorbed by heating the collection tubes (≈350°C), and desorbed gases are forced through a "transfer tube" and over a heated catalyst bed. When the hollow collection tube is heated, NH_3 and HNO_3 are released. The NH_3 remains as gaseous NH_3 and HNO_3 is released as NO_2 and NO. The transfer tube is simply a hollow collection tube held initially at room temperature, and serves to re-collect the NH_3, thereby separating it from the NO_2 and NO released from the HNO_3. The NO_2 resulting from the HNO_3 is not affected by the transfer tube and is converted to NO in the catalyst bed. The first step in the analysis is completed with detection of the NO originating from HNO_3 via the NO_x analyzer. The second step is initiated by heating the transfer tube to thermally desorb NH_3, which is oxidized to NO in the catalyst bed and subsequently detected in the NO_x analyzer. In a similar manner the aerosol components collected in the packed tubes are analyzed in a two-step process. Heating the aerosol collection (packed) tubes releases NH_3 from the ammonium-containing compounds and NO_2 from the nitrate compounds. Separation and conversion of each species to NO and detection of NO are identical to the processes described for the hollow tubes.

The sensitivity of the technique, as for any collection technique, is determined in part by the size of the sample, which in turn depends on sample flow rate,

collection time, and collection efficiency. Collection efficiencies greater than 95 percent have been demonstrated, and with commercially available NO_x detectors, detection limits of 1 to 3 ng/sample (≈0.1 ppbv for 20-liter sample at STP) have been reported, depending upon the species. It is expected that these detection limits could be improved through the use of state-of-the-art NO_x detectors. (See section entitled Chemiluminescence Techniques.) This would result in shorter collection times and/or measurements at lower ambient levels for the same sampling time. Currently, for on-line analysis, approximately 12 minutes are required to complete the analysis for four species. Collection tubes can be sealed and analyzed off-line at a later date.

The major disadvantage of the tungstic acid technique is similar in nature to that of many other atmospheric sampling techniques, namely the potential of unknown interferences from other atmospheric species. Studies strongly suggest a high degree of specificity to gaseous NH_3 and HNO_3 and the ability to identify the relative contributions of the ammonium and nitrate aerosols. Laboratory studies, although not exhaustive, indicate that alkylamines are the only significant source of interference (out of approximately 20 compounds considered). Another disadvantage of the technique is contamination of the collection tubes. Contamination or poisoning of packed and hollow tubes has been identified as a specific problem (Braman et al., 1982; McClenny et al., 1982; Harward et al., 1982). Contamination results in a net decrease in the collection efficiency and can only be recognized via calibration. No definite studies have been reported to quantify the contamination mechanism, but its potential impact on measurement interpretation clearly requires frequent calibration.

Gas Chromatography.- Gas chromatography is a frequently used analysis tool for measurement of trace gases in the atmosphere. Depending upon the column separation techniques and the choice of detection, it can be a sensitive and selective measurement approach. Gas chromatography using electron capture detection has been applied to PAN detection in the atmosphere (Singh and Salas, 1983a). Successful PAN detection using gas chromatography normally requires a three-step procedure:

1. Selective removal of water from the sample

2. Cryogenic preconcentration of the sample prior to analysis by electron capture

3. Development of a portable continuous primary PAN calibration system

PAN has been measured at concentrations of 5 pptv. A real-time electron capture gas chromatograph (EC-GC) instrument has been flown in the free troposphere to an altitude of 8 km. The technique has been tested and validated within an estimated accuracy of ±20 percent. In addition, a continuous PAN calibration system has been devised (Singh and Salas, 1983b). With refinement of the technique and procedures, 1-pptv levels of detection are feasible.

Assessment of Techniques

In order to summarize and assess the status of N_xO_y measurement techniques, the workshop participants prepared a series of tables (Table V to XI) in which the status and capabilities of the various techniques were listed. Each table entry was discussed during the workshop and thus represents a consensus among the participants. No attempt was made to compare or rank the various techniques as to their applicability to global tropospheric measurements. Ten instrument or status parameters were

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selected as the basis for the assessment and are shown as column headings in the tables. A table was generated for each N_xO_y species for which measurement techniques were discussed. An explanation of the column headings and entries is given below.

Status

Four status classifications were established. Any technique in the concept stage and not yet incorporated into instrument hardware was assigned status 1. Techniques for which instruments existed and were in some form of laboratory testing were assigned status 2 (e.g., benchtop or breadboard instruments). Status 3 techniques were those judged to be ready for field testing or currently being field tested. Status 3 does not signify that all lab testing is complete or that field tests have started. Techniques previously used in the field to gather scientific data were assigned status 4. Status 4 is analogous to an operational classification.

In Situ/Remote

Techniques were classified as being applicable to either an in situ or a remote sensor.

Sensitivity and Time Resolution

Entries in these two columns are related. Sensitivity is the lowest detection limit of the technique and unless noted otherwise is at a signal-to-noise ratio of 2. Time resolution is the time period over which the signal is observed (or averaged) in order to attain the stated sensitivity. For status 2, 3, and 4 techniques, the sensitivity entry is that for the existing instrument. An entry in parentheses (if shown) is an anticipated sensitivity, assuming improvement of known instrument shortcomings. For status 1 techniques, sensitivity either is listed as TBD (to be determined) or an estimate based on theoretical and conceptual analysis is given. In the time resolution column and for remote techniques, the path length for which the sensitivity and time resolution entries are applicable is shown in parentheses.

Accuracy

Accuracy is the difference between the measured value and the "true" value. As will be discussed later in the section entitled Measurement Validation, "true" value is a difficult quantity to define and warrants discussion in itself. A TBD entry implies that the accuracy of the technique is yet unspecified.

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Precision

Precision is a quantity that expresses the ability of a given technique to reproduce its own results under conditions of constant concentration and constant environment. It reflects the random errors inherent in the measurement technique and hence is concentration dependent (i.e., precision at a concentration level twice the detection limit of the technique is different than at a concentration 10 times the detection limit). Precision values shown in the tables are for concentrations 100 times the stated sensitivity of the technique. A TBD entry indicates that the precision of the technique is yet unspecified.

Interferences

Listed here are such possibilities as species, processes, and environmental conditions which cause artifacts, positive or negative competing output signals, or misinterpretation of results. A "none known" entry is interpreted to mean

1. That studies to date have revealed no major interferences
2. That studies to date of expected interferences have shown these not to be a major problem in reducing the data
3. That theoretical considerations suggest no significant interferences exist

It should be noted that one can never be confident that a technique is completely interference free. One can only evaluate the technique for known or suspect interferences. Thus a "none" entry is not used in the tables. The TBD entry signifies that interference studies or considerations have not yet been performed.

Calibration

Table entries indicate the lowest concentrations at which test gas mixtures have been prepared for purposes of technique calibration. An "NA" entry has several interpretations. For a remote-sensing technique it implies "not appropriate." For a status 1 or 2 technique it implies "not available" as a result of not yet being at that stage of development. For a status 3 or 4 technique, it implies "not available" as a result of the absence of reliable standards or the fact that the technique is not amenable to calibration with gas mixtures.

Environmental Constraints

This column identifies those environmental conditions which present operational problems for the technique. Environmental constraints differ from interferences in that they either limit or invalidate the applicability of the technique, or change the baseline sensitivity, calibration, accuracy, or precision of the technique.

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Platform Usage

Techniques were considered for applicability to sampling on the ground, aboard ships, or from an aircraft. An "all" entry implies that the technique is suitable for all three applications. A technique need not have been operated or designed for all three applications in order to be designated as "all."

Comment

This column is used to present additional information about the technique which could not be included under one of the general columns.

Table V - Assessment of NO Techniques

Technique	Status	In situ/ remote	Sensitivity	Time resolution	Accuracy, percent	Precision, percent	Interferences	Calibration	Environmental constraints	Platform usage	Comment
Chemiluminescence	4	In situ	5 pptv	1 sec	15	5	Terpenes, ethylene	7 pptv	Water vapor	All	Sensitivity is dependent on water vapor concentration present.
Single-photon laser-induced fluorescence	4	In situ	240 (60) pptv 30 (8) pptv 4 (1) pptv	1 sec 1 min 1 hr	15	10	White fluorescence	20 pptv		All	
Two-photon laser-induced fluorescence	2	In situ	96 pptv 4.5 pptv 0.6 pptv	1 sec 1 min 1 hr	15	2	TBD	400 pptv		All	
Lidar laser-induced fluorescence	3	Remote	10 pptv 5 pptv 3 pptv	(0.1 km) 1 sec (4 km) (8 km)	15	2	Solar flux, white fluorescent noise	NA	Clouds, heavy aerosol loading, temperature changes	All	Laser energy of ~1 mJ at 226 nm
Tunable-diode laser	3	In situ	2.4 ppbv 300 (30) ppbv	1 sec 1 min	10	5	None known	6 ppbv	Temperature changes	All	
Resonant-ion laser	2	In situ	10 (1) ppbv	1 sec	TBD	TBD	TBD	NA	Temperature changes	All	Technology limited due to need for tunable UV laser with more energy.
Long-path UV absorption	4	Remote	100 pptv	5 min (1 km)	20	5	None known	NA	Heavy aerosol loading	Ground	

Note: All concentrations measured by volume.

Table VI - Assessment of NO_2 Techniques

Technique	Status	In situ/ remote	Sensitivity	Time resolution	Accuracy, percent	Precision, percent	Interferences	Calibration	Environmental constraints	Platform usage	Comment
Chemiluminescence	4	In situ	10 pptv	1 sec	30	5	Converter dependent[a]	25 pptv	Water vapor	All	(b)
Photofragmentation laser-induced fluorescence	2	In situ	96 pptv 12 pptv 1 pptv	1 sec 1 min 1 hr	15	5	TBD	4 pptv	Temperature changes	All	Laser energy and repetition rate are limiting current technology.
Multiphoton ionization	1	In situ	1 pptv	1 sec			RNO_2	NA	Temperature changes	All	UV laser energy and repetition rate are limiting current technology.
Tunable-diode laser	3	In situ	300 pptv	1 min	10	5	None known	10 pptv	Temperature changes	All	
Long-path UV absorption	4	Remote	100 pptv	1 min (1 km)	20	5	None known	NA	Heavy aerosol loading, high O_3 concentrations	Ground	Path length is limited by visibility, aerosol loading, and ozone concentration.
Photothermal		In situ			TBD				Temperature changes		
1) photoacoustic	2		200 pptv (1-5 pptv)	1 sec		5	H_2O aerosols	1 ppbv		All	CO laser
2) resonant-cell photoacoustic	2		200 pptv (1-5 pptv)	100 sec (1-100 sec)		5	NO_3, O_3 aerosols	1 ppbv		Ground	Ar laser
3) Zeeman modulated	1					TBD	None known	NA		All	CO laser

[a] NO_2 detection is via thermal, chemical, or photodissociation of NO_2 to NO.

[b] Sensitivity is dependent on water vapor concentration present. Converters may convert some N_2O_5 or PAN, thus producing artifacts or interferences.

Note: All concentrations measured by volume.

Table VII - Assessment of NO_3 Techniques

Technique	Status	In situ/ remote	Sensitivity	Time resolution	Accuracy, percent	Precision, percent	Interferences	Calibration	Environmental constraints	Platform usage	Comment
Photofragmentation laser-induced fluorescence	1	In situ	22 pptv 3 pptv 0.3 pptv	1 sec 1 min 1 hr	TBD	10	TBD	NA	Temperature changes	All	Laser repetition rate limits current technology.
Long-path UV absorption	4	Remote	1 pptv	5 min (10 km)	30	5	None known	NA	Water vapor, heavy aerosol loading	Ground	Path length is limited by visibility and aerosol loading.

Note: All concentrations measured by volume.

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Table VIII - Assessment of NO_3^- Aerosol Techniques

Technique	Status	In situ/ remote	Sensitivity	Time resolution	Accuracy, percent	Precision percent	Interferences	Calibration	Environmental constraints	Platform usage	Comment
Filter	4	In situ	4 pptv	1 hr	30	10	HNO_3 H_2SO_4	NA	Heavy aerosol loading	All	
Tungstic acid	3	In situ	70 (10) pptv	20 min	20	10	TBD	NA		All	Analysis requires 10-20 min.

Note: All concentrations measured by volume.

Table IX - Assessment of HNO_2 Techniques

Technique	Status	In situ/ remote	Sensitivity	Time resolution	Accuracy, percent	Precision, percent	Interferences	Calibration	Environmental constraints	Platform usage	Comment
Photofragmentation laser induced fluorescence	1	In situ	112 pptv 14 pptv 2 pptv	1 sec 1 min 1 hr	TBD	10	TBD	NA	Temperature changes	All	Laser repetition rate limits current technology.
Long-path UV absorption	4	Remote	20 pptv	10 min (10 km)	20	5	None known	NA	Visibility, heavy aerosol loading	Ground	Path length is limited by visibility and aerosol loading.
Condensation	4	In situ	15 pptv	1 hr	TBD	5	PAN	NA	Temperature changes, heavy pollution	All	Cannot distinguish hydrolysis products.

Note: All concentrations measured by volume.

Table X - Assessment of HNO_3 Techniques

Technique	Status	In situ/ remote	Sensitivity	Time resolution	Accuracy, percent	Precision, percent	Interferences	Calibration	Environmental constraints	Platform usage	Comment
Chemiluminescence	4	In situ	200 pptv	10 sec	TBD	TBD	TBD	NA		All	
Tunable-diode laser	3	In situ	3 ppbv (240 pptv) 300 (30) pptv	1 sec 1 min	10	5	None known	6 pptv	Temperature changes, heavy aerosol loading	All	
Filter	4	In situ	2 pptv	1 hr	30	2	NH_4NO_3, aerosols, N_2O_5	15 pptv	Heavy aerosol loading	All	
Condensation	4	In situ	20 pptv	1 hr	TBD	5	Aerosols, aqueous-phase reactions	NA	Temperature changes, heavy aerosol loading	All	
Fourier transform IR	4	In situ	10 ppbv	1 min	20	5	None known	NA	Temperature changes, heavy aerosol loading	All	
Tungstic acid	3	In situ	70 (10) pptv	20 min	20	10	TBD	NA		All	Analysis requires 10-20 min.

Note: All concentrations measured by volume.

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Table XI - Assessment of PAN Techniques

Technique	Status	In situ/ remote	Sensitivity	Time resolution	Accuracy, percent	Precision, percent	Interferences	Calibration	Environmental constraints	Platform usage	Comment
Chemiluminescence	2	In situ	TBD	TBD	TBD	TBD	NO, NO_2, N_2O_5	NA		All	Selectivity of PAN converter must be verified.
Fourier transform IR	4	In situ	1 ppbv	10 sec 100-m path	25	10	TBD	NA		All	
Gas chromatography	2	In situ	5 pptv	1 min	15	15	TBD	40 ppbv		All	

Note: All concentrations measured by volume.

Current Capabilities Versus Measurement Requirements

This section summarizes the current status of measurement capabilities for N_xO_y species relative to required measurement needs. Several assumptions are made in terms of the measurement requirements (Table I) and anticipated measurement scenarios.

1. Measurement scenarios are anticipated to be aircraft missions at flight speeds of approximately 400 km/hr (≈250 MPH).

2. Measurement scenarios are for the scientific purposes of obtaining quasi-equilibrium concentrations as a function of location and altitude in the troposphere. As such, two flight scenarios are considered:

(a) Constant altitude at 400 km/hr to obtain horizontal spatial resolution

(b) Constant ascent or descent flights at 150 m/min for vertical spatial resolution

3. Scientific scenarios for flux measurements and/or chemical kinetics are not considered. Measurement requirements in terms of time response and/or accuracy are more stringent than those used to obtain quasi-equilibrium concentrations.

4. Five independent samples or "averages" are required to define a species concentration at a given location in the troposphere.

NO Detection

Based on the guidelines of Table I and the assumptions above, NO must be measured at the pptv level with a horizontal time response of approximately 6 minutes and a vertical response of approximately 20 seconds. As shown in Table V, there are a number of techniques which can meet these requirements, assuming they are developed to their potential and function as stated. Most of these techniques are well advanced in their development (status 3 or 4 in Table V). The NO techniques considered should provide ample measurement capabilities to meet global NO measurement requirements.

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NO_2 Detection

NO_2 measurement requirements are identical to those for NO (pptv level, 6-minute or 20-second response). As shown in Table VI, only a few meet these requirements. Of these, only chemiluminescence is status 4. As discussed earlier, this technique requires the use of NO_2-NO converters and multimode measurement cycles. It can be concluded that although several techniques will potentially be developed to the level of performance required, a proven NO_2 technique is not currently available to meet the 20-second response characteristic for vertical measurements. Continual development of those techniques in Table VI should result in an NO_2 technique suitable for global monitoring.

NO_3 Detection

As shown in Table VII, only two techniques are being considered for NO_3. One, a status 4 technique, is a remote sensor requiring a 10-km path length for pptv level detection and is not suitable for aircraft applications. The second is status 1 and as such is only a concept. Clearly an NO_3 detection technique is not available for global tropospheric applications and few are being actively developed.

NO_3^- Aerosols

Only two techniques are available for NO_3^- aerosol measurement. (See Table VIII.) Although they are advanced in their development program (status 3 and 4), both are indirect techniques, requiring collection sampling and subsequent chemical analysis. Both, by their nature, will experience shortcomings in the area of interferences. Currently, neither can be considered operational at detection levels required by global tropospheric sampling, but with additional field testing both may be proven adequate for global measurement needs.

HNO_2 Detection

Of the three techniques considered (Table IX), two are status 4, but neither can meet measurement requirements. The ground-based long-path UV absorption is a remote sensor with the 10-km path length required to reach 20 pptv levels. The condensation technique requires a 1-hour resolution (for 15 pptv) and cannot be calibrated in the present configuration. The status 1 technique is only a concept and is thus not yet in a feasible design stage. A measurement technique does not exist for HNO_2, nor does it appear that one will surface in the near future without additional emphasis by a scientific need.

HNO_3 Detection

As illustrated in Table X, HNO_3 measurement requirements are somewhat different. Detection at the pptv levels is required, but on a horizontal spatial response of approximately 15 minutes and a vertical response of approximately 1-1/2 minutes. As shown in the table, six different techniques (all status 3 and 4) are available for HNO_3 measurements. Of these, only the two status 3 techniques (tunable-diode laser and tungstic acid) show promise for global tropospheric applications. Both require more hardware and field testing before their capabilities can be defined.

PAN Detection

Although three techniques (Table XI) are available for consideration, only two have pptv detection capabilities. A PAN-specific NO converter (chemiluminescent) does not currently exist, although it is feasible in principle. This method has the

potential advantage of providing continuous real-time measurements. The electron-capture gas chromatograph (EC-GC) real-time technique is further along in development and has been successfully tested to 8-km altitudes.

Table XII summarizes the expected timetable for N_xO_y species measurement capabilities. Time periods are somewhat speculative, but are estimates based on existing technology, program funding to do instrument development, and anticipated scientific "pressure" for a given species measurement. Many of the status 1 and 2 techniques and even some status 3 and 4 techniques are low-key activities supported by institutional funds. In these cases, further development will be slow (or nonexistent) without definition of definable programmatic needs and funding.

Table XII - Projected Timetable for Development of N_xO_y Measurement Techniques

Species	Class I[a]	Class II[b]	Class III[c]	Class IV[d]
NO	✓			
NO_2		✓		
NO_3			✓	
NO_3^- aerosol		✓		
HNO_2			✓	
HNO_3		✓		
PAN		✓		
HNO_4				✓
N_2O_5				✓

[a]Class I - Technique existing and development funded, available now or in 1984.

[b]Class II - Sufficient scientific need (general community), some funding, available by 1986.

[c]Class III - Scientific need not strongly emphasized, little direct funding (some institutional support), available by 1986 only if emphasis increased.

[d]Class IV - No technique being actively pursued.

Technology Required To Improve Current Capabilities

For the techniques of trace-gas detection of N_xO_y which have already been successfully implemented in the field, methods to improve the current instrumentation technology have been identified. These improvements, if successfully implemented, would result in advances in the current instrumentation technology. In the following sections, these suggested improvements are listed for the current field techniques (status 3 or 4 in the assessment tables).

$NO-O_3$ Chemiluminescence

The $NO-O_3$ chemiluminescence technique would be improved by a redesign of the photon collection and detection systems. The photon collection efficiency is determined by the reaction volume design and the photon detection efficiency is determined by the choice of interference filter and photomultiplier tube. The identification and elimination of the background signal and the reduction in signal integration time will directly improve the signal-to-noise ratio.

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In the detection of other species (principally NO_2 and HNO_3), improvements in the conversion processes are possible. In the photodissociation of NO_2, an improved UV lamp output would increase conversion efficiency. An intercomparison among the photolytic, pyrolytic, catalytic, and denuder-tube conversion techniques will assist in validating these techniques. Research on all converters will identify interfering species, if any.

Single-Photon Laser-Induced Fluorescence (SP-LIF)

The technique of SP-LIF for detection of NO will benefit from improvements in laser technology. A laser that can provide higher energy per pulse ($\approx$4 mJ cm^{-2} at 226 nm) and at a higher repetition rate will improve the signal in this technique. The current development of a two-photon laser-induced fluorescence technique will significantly improve the detection signal-to-noise ratio over the SP-LIF technique.

Tunable-Diode Laser (TDL)

Tunable-diode laser detection of NO, NO_2, and HNO_3 will be improved by increased diode laser power and by new diode lasers that have increased stability and reliability. Efficient refrigeration techniques suitable for field use are desirable. A redesign of TDL optical systems to reduce optical noise due to etalon effects will improve the system signal-to-noise ratio significantly.

Long-Path Absorption

The technique of long-path UV and visible absorption for the detection of NO, NO_2, HNO_2, and NO_3 will be improved by increasing the light source intensity. Increased intensity will allow a longer path length to be used. In addition, larger optics, including the field and receiving mirrors, will improve the absorption signal. Improvement in the accuracy of independent measurements of species absorption coefficients will directly improve the accuracy of the long-path technique.

Filter

The filter technique for the detection of HNO_3 and NO_3^- aerosols will be improved by increased ion chromatography sensitivity. Improved sensitivity will shorten filter integration time significantly. For HNO_3 detection, improvements in HNO_3 permeation devices will decrease the present 20-percent uncertainty in the filter technique.

Condensation

The condensation technique for the measurement of HNO_3 and HNO_2 will be directly improved by advances in the sensitivity of ion chromatography. The technique will also be improved by a redevelopment to provide thermoelectric cooling and increased automation. A flow-through system will allow direct calibration, increase sample rate, and elucidate the contribution of interferences.

Gas Chromatography

The technique of PAN detection with gas chromatography and an electron capture detector will be improved by a more rugged instrument design for field use and a more reliable calibration method. In addition, modifications may be required to match the dynamic range of the detection system to that of PAN concentration in the troposphere.

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Other Techniques

The two remaining status 4 techniques, lidar, laser-induced fluorescence and Fourier transform infrared, are both remote sensors, and as such any improvement in light source intensity and optical receiver efficiency will result in better detection levels. The lidar technique is currently being evaluated in an engineering flight program from which potential instrument improvements will be defined. The Fourier transform infrared technique, which still can be improved, is not believed to have sufficient sensitivity for global tropospheric (clean) concentrations.

FUTURE INSTRUMENT NEEDS

Nonexistent or Inadequate Capability

Of the N_xO_y species considered by the workshop (NO, NO_2, NO_3, NO_3^- aerosol, HNO_2, HNO_3, HNO_4, PAN, and N_2O_5), only two species, HNO_4 and N_2O_5, were identified as having nonexistent measurement capabilities. It was the consensus that measurement techniques for these two species, which could be used onboard aircraft making "clean" tropospheric concentration measurements, are not available in either a developmental or a conceptual status. The priority for developing instruments to measure HNO_4 and N_2O_5 as well as other N_xO_y species was not considered by the workshop and should be based on the importance given to these molecules by the atmospheric modeling community. For the other N_xO_y species considered, it was felt that techniques discussed at the workshop had the potential to meet global tropospheric measurement needs, assuming that techniques could be developed to their anticipated full potential and verified through field testing. Field intercomparison tests were highly recommended as a vehicle to accomplish verification.

It was also a consensus that although techniques for NO_2, HNO_3, PAN, and NO_3^- aerosol are not currently adequate, within the near future these will be developed to an adequate capability. The current stage of development of instruments for these species and pressure from the scientific community will provide an emphasis to complete development and testing of the instruments. Concern was voiced that for species such as NO_3 and HNO_2, measurement techniques will not be developed to a level adequate to meet global tropospheric needs. In these cases, although a few techniques exist in some stage of development, more programmatic interest and support will have to occur before these and yet-to-be considered ideas will advance.

An additional concern discussed at the workshop was that for most species (with the exception of NO and NO_2), only a few concepts are being developed which meet global monitoring needs. Since each technique, whether a direct or indirect measurement of the species, has systematic errors which are difficult to identify and quantify at the low concentrations of interest, some consideration should be given to developing different measurement concepts. Measurement (field or intercomparison studies) of a species with techniques using different concepts (and thus different systematic errors) will ensure validation of the measurement as well as acceptance by the scientific community. Again, the importance of a species as determined by the modeling community can provide guidelines in interpreting this requirement.

Fundamental Research Studies

Two basic technology areas were identified which are limiting the capabilities of current N_xO_y measurement techniques: standards and calibration procedures, and

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laser development. There was total agreement among the participants that suitable technology advances in these two areas would greatly enhance N_xO_y measurement capabilities at "clean" tropospheric concentration levels.

In the area of calibration standards and procedures, it was noted that industry standards definitely exist for one N_xO_y species (NO) and possibly for a second species (NO_2). Even for these two species, standards are at the ppmv level (a factor of 10^4 to 10^5 higher than the pptv concentrations measured in the global troposphere), and various gas dilution schemes must be used to obtain calibration at measurement levels. Gas cylinder standards (certified reference material or standard reference material) are only available from the National Bureau of Standards (NBS) or a few commercial gas vendors at a concentration of approximately 10 ppmv or higher. For other species (for example, HNO_3 and PAN), accepted standards and procedures do not exist, and each researcher must attempt to develop those standards and procedures required by his measurement. Although each instrument researcher is genuinely concerned with the preparation of calibration standards and procedures to test and evaluate his measurement technique, these efforts are limited and will have little impact on the basic technology. Until reliable standards and calibration procedures are developed and agreed upon the scientific community, the full potential and application of many current N_xO_y measurement techniques will not be realized. In addition, many existing techniques with known artifact, background, or interference effects can be improved if lower concentration standards were available and were incorporated into the measurement schemes. It was the general opinion of the workshop participants that the standard and calibration procedure area is a basic technology need applicable to species other than N_xO_y, and thus requires basic research studies.

The second technology area, laser development, was noted by most instrument researchers using laser measurement schemes to be a limiting factor in their instrument development. Most researchers suggested an improvement of measurement capability with some fundamental laser improvements (i.e., either improved laser capability or more rugged, environmental conditioned lasers). Requirements or needs differed among the participants, depending on their measurement schemes, but were in the areas of higher repetition rates, higher energy, more options on wavelength selection, longer lifetimes, and environmental hardiness to function better in an aircraft environment. Although specific needs or applications were not discussed, a few statements of the type of needs were identified. Excerpts from these statements are listed below.

1. "A laser that can provide higher energy per pulse at 226 nm and at a higher repetition rate will improve the signal in this technique."

2. "Detection will be improved by increasing diode laser power and by new diode lasers that have increased stability and reliability."

3. "To get to the UV is quite troublesome with dye lasers - UV laser development is necessary."

Most participants using laser-based detection schemes listed temperature and associated laser stability as a concern for field operations, particularly aircraft.

Promising New Technologies

Several proposed new measurement techniques for N_xO_y were presented and more detailed descriptions of these methods can be found in other sections of this

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document. An indirect method, the tungstic-acid denuder tube NO-O_3 chemiluminescent method, was proposed for measurement of HNO_3. The other proposed instrumental techniques were direct measurement methods based on laser spectroscopy. Laser spectroscopic methods have the potential for high sensitivity and selectivity for direct measurement of molecules in complex mixtures. Several laser methods for trace N_xO_y tropospheric measurements are presently undergoing laboratory evaluation and testing. When these laser methods establish the required sensitivity, selectivity, and lack of interference comparable to currently developed indirect N_xO_y measurement methods, they can be used for intercomparison tests. These laser methods would have an advantage for tropospheric measurements in that they are direct measurement techniques and similar laser technology is already being used to measure tropospheric species other than N_xO_y, such as O_3, SO_2, and OH.

Specific new laser methods proposed at this meeting were the laser-induced fluorescence methods for NO, NO_2, NO_3, and HNO_2. These techniques include single-photon (SP-LIF), two-photon (TP-LIF), and photofragmentation (PF-LIF). Currently the SP-LIF technique for NO is the most developed method and should be ready for field demonstration in 1983.

Laser ionization methods, both multiphoton laser ionization and laser resonant ionization (both detecting NO and/or NO_2), are new techniques. Although these laser ionization techniques are in the early stages of development and have not yet been studied for mixtures simulating tropospheric conditions, their sensitivity and selectivity for measurements of trace N_xO_y are anticipated to be better than those of the in situ LIF methods. Tunable-diode IR laser absorption techniques are another promising new technology which is applicable for measuring HNO_3, NO, and NO_2. The full potential of this technique is somewhat dependent on future laser developments and availability.

NO_2 measurements using photothermal (photoacoustic phase fluctuation optical heterodyne) techniques and HNO_2 and HNO_3 measurements using the condensation technique are examples of refinements to existing fundamental measurement approaches which are being considered and which offer promising improvement in detection of those species.

MEASUREMENT VALIDATION

Introduction

In order to certify and validate measurement techniques for trace gases in the atmosphere, both instrument calibrations and intercomparisons are required. In the final analysis, the criterion by which the accuracy of the measurement of an atmospheric compound is established is intercomparisons of measurements made by instruments using different principles of detection. Such measurements should be carried out in the field and subjected to a wide variety of atmospheric concentrations. A desirable prerequisite for field intercomparisons is instrument calibrations using validated procedures and traceable standards.

To date, a limited number of intercomparisons have been attempted on the instruments used to measure atmospheric N_xO_y compounds. These intercomparisons (Spicer et al., 1982; Howes et al., 1981) involved simultaneous operation of two or more instruments using different detection methods. Measurements were carried out for NO, NO_2, and HNO_3 in urban environments containing relatively high levels of these compounds. As such, these intercomparisons failed to address the levels of sensitivity, selectivity, and accuracy which are required to measure N_xO_y compounds in the clean

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troposphere. For this reason, a significant goal of tropospheric research efforts should be to validate the critical measurements of N_xO_y compounds through:

1. A well-developed in situ calibration scheme for each individual instrument
2. Intercomparisons of calibration standards
3. An extensive program of field intercomparisons carried out in the clean troposphere

Calibration

Broadly speaking, measurement techniques can be categorized as in situ or remote. The calibration and validation approaches discussed in this document apply to in situ techniques. Remote techniques are of interest; however, based on the current state of the art for the N_xO_y species and clean tropospheric measurement requirements, this interest is as a secondary means of intercomparison with in situ techniques. At a somewhat later stage and at a more basic level, the question of the limits of intercomparability of the in situ and remote measurements must also be addressed.

The calibration and validation of remote methods involve three questions. The first concerns the accuracy with which the basic spectroscopic parameters are determined (i.e., spectra, absorption coefficient, line shape, line broadening factors, etc.). The second concerns how many spectral elements are determined, and thus how much noise rejection the method is capable of. The third depends on the distribution of the compound of interest through the path and the degree to which spectral interference parameters are known through the path.

In regard to in situ techniques, the best insurance for consistent, reliable measurements with a field instrument is provided by frequent in situ calibrations. The calibration gas standards should be stable and accurate, and the calibrations for an in situ technique should be made with the calibration gases subjected to the same gas flow path through the instrument as exists in the sampled air. Moreover, standard addition and dilution techniques should be available to allow the linearity of the instrument, wall loss processes, and matrix gas (interference) effects to be checked. For NO and NO_2, this rigorous approach is presently possible and should be required of the instruments measuring these compounds. The remaining N_xO_y compounds of interest are not sufficiently well behaved to allow this calibration approach. Calibration procedures for nitric acid have been developed. Thermally unstable N_xO_y compounds such as PAN and N_2O_5 can be formed but are difficult to store for any length of time. On-line preparation and dilution systems may be required. In the case of PAN, such a system is already operational. For HNO_2, NO_3, and HNO_4, which are quite reactive and unstable, calibration procedures have not yet been established. Until the calibration procedures for these species are more fully developed, it is not possible to address the problems that may be involved in the calibration and validation of the instruments measuring these compounds.

Accuracy

The assessment of accuracy (i.e., the difference in the measured value versus the "true" value) in any concentration measurement is acknowledged to be of pivotal importance to the successful use of field data in tropospheric investigations. The

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difficulty in defining such a quantity lies in the problem of defining the "true" value. This is particularly true for measurements in the global troposphere, where concentrations tend to be very low compared to concentrations of reliable gas standards. The approach used by most investigators is that of defining accuracy in terms of a "best estimate" of the overall magnitude of the systematic errors in a given technique. This, in many cases, is reported as a function of different atmospheric environmental conditions. These "best estimate" values must be used with caution.

The preferred approach in defining instrument accuracy involves the evaluation of a quantity which we may define as the "empirical true value." The "empirical true value," for a given set of atmospheric conditions, may be defined as the mean value of the concentration as measured by several different instrument types where each instrument type is likely to have a different inherent set of systematic errors. The confidence level in this "empirical true value" is thus dependent on the number of independent techniques used in the assessment and the standard deviation in the mean value of all concentration measurements. Further iterations of this intercomparison process can ultimately result in the identification and correction of many of the systematic errors in different instrument types. In this manner, an improved "empirical true value" having a smaller standard deviation should emerge. Such convergence to a final "empirical true value" has been a rarity in the atmospheric community. This appears to be the result of both a lack of an adequate number of different measuring techniques and the absence of organized efforts to carry out long-term field intercomparisons.

Precision

The general definition of precision is that it is a quantity that expresses the ability of a given instrument to reproduce its own results under conditions of constant concentration and constant environment. Thus it reflects the random errors inherent in the measurement technique.

The precision of an instrument measurement is most frequently referenced to laboratory conditions (i.e., constant environment) and typically is specified at the limit of detection as well as at some elevated concentration where the system is not signal limited. Thus, if one defines the limit of detection of a species as that concentration level at which the signal-to-noise ratio is 2, then by definition the precision is given as ±50 percent. Normally precision is more meaningful if defined at a concentration somewhat higher than the limit of detection of the technique. For the assessment tables presented earlier, the authors specified the precision for each technique at a concentration 100 times the detection limit.

It may be argued that the precision given for a laboratory setting may not reflect the precision that might be obtained under harsh environmental conditions. In a real-world sampling environment, the evaluation of the "field precision" for a given instrument requires that the fluctuation in the concentration in time be small when compared to the precision estimated for the technique under controlled laboratory conditions. In determining a "field precision," it is important to consider properly the various sources and sinks of the species in question in order to ensure that what is measured is field precision rather than atmospheric variability.

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Calibration Standards for NO, NO_2, and HNO_3

The presently accepted calibration standard for NO is a standard gas mixture containing up to 1 ppmv of NO in N_2. These standards are prepared by static dilution and should be traceable to NBS reference standards. Generally, standards are available directly from NBS or commercial gas vendors. In each case, the SRM (standard reference material) is traceable to NBS in both concentration and stability (lifetime). Permeation tubes provide a reliable standard for NO_2. The emission rates of the permeation tubes are determined gravimetrically. NO_2 permeation tubes are also available commercially for a wide range of emission rates, temperature ranges, and gas flow rates. In addition, gas phase titration ($NO + O_3 \rightarrow NO_2$) can be used to intercompare NO and NO_2 standards. Permeation and capillary diffusion tubes are also available for HNO_3. Because of the decomposition of nitric acid emitted from these tubes, the rate of emission of HNO_3 has an uncertainty of approximately 20 percent. The remaining N_xO_y compounds are unstable, and presently no calibration standards are available.

Intercomparison

Calibration Standards

The first level of instrument intercomparison involves the informal exchange of aliquots of calibration standards used by the various techniques. At the same time, though at a somewhat more formal level, the lead agency sponsoring an intercomparison should provide a series of aliquots of an unknown concentration at levels comparable to the calibration standard. These double-blind intercomparisons will be used to establish the precision and accuracy of instrument calibrations. The virtue of an exchange of aliquots mixed to large concentrations (1 ppmv) of NO is that reasonably small quantities of gas are involved at levels known to be stable. At lower levels (<<1 ppmv NO) the question of sample stability becomes a factor. These lower-level concentrations can be generated by dynamic dilution of the supplied reference standards. The exchange of stable aliquots of NO_2 at 1-ppmv concentration levels are not yet possible. Further work on the certification of the stability of NO_2 in containers (and NO at smaller concentrations) should be undertaken. Exchange of permeation sources for NO_2 and HNO_3, including a thermostated permeation tube along with carrier gas, should be investigated as a means of allowing this primary level of intercomparison of instruments measuring NO_2 and HNO_3.

Field Intercomparison

A full field intercomparison of measuring techniques is needed to provide validation of measurement capability for a given N_xO_y species. The intercomparisons will be most meaningful when they include techniques utilizing different detection principles. These instruments will presumably have different responses to interferences and artifact-producing agents. The ability of these instruments to obtain agreeable measurements over wide ranges of concentrations, including those typical of the clean troposphere, will constitute certification. In addition to the in situ techniques, a remote measurement, if available, would be desirable to provide secondary validation and a basis on which to generalize the measured concentrations obtained by the in situ techniques. In situ techniques expose samples to instrument walls, whereas remote techniques do not. In addition, remote sensors (for example, long-path absorption techniques) can be calibrated at relatively high concentrations using gas cell calibration approaches. Such comparisons then could expose systematic errors introduced by in situ techniques.

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The intercomparison protocol should be set down in a written document stating the procedures to be followed in the intercomparison and the basis for comparison. This document should specify the sampling inlets to be used (common or individual, material size, flow rate, etc.) and the logistics of the sampling facility and ancillary environmental and meteorological data to be supplied. The raw data from each measurement should be supplied to the sponsor of the intercomparison in a specified format, along with sufficient information to process the data. At the conclusion of the intercomparison, the sponsoring agency should provide a mathematical critique of the level of agreement achieved by the intercomparison.

The sponsoring agency should consider providing all calibration standards to ensure uniformity and should also provide a dynamic dilution system. This system will provide gas samples to test sampling linearity and response in each instrument. It is recommended that the principal investigators involved process the raw data immediately. The ability to establish disagreements quickly will provide the most favorable situation to find and remedy any discrepancies.

In addition to standard local meteorological and environmental data, additional meteorological information should also be made available. This includes data from weather balloons to establish temperature, dew point, wind speed and direction at altitudes above the intercomparison location, and air trajectory profiles indicating the origin and history of the air masses that are sampled. These additional data will be useful in understanding the sources of the detected N_xO_y as well as the intercomparison of remote and in situ measurements.

Criteria of Success

The success of the intercomparison should be established at three levels. First, if in the opinion of the principal investigators their techniques were properly functioning (i.e., able to detect calibration standards with nominal signal-to-noise levels) during the period of the intercomparison, then the intercomparison will be considered successful independent of the agreement in the results. The primary goal of the initial intercomparison will have been accomplished. On the second level, if the agreement among instruments is adequate to suggest that measurements can be made within a range of uncertainty sufficiently small to answer important questions of atmospheric chemistry, the instruments will be considered field operational. Finally, the instrument will be considered to be fully validated if the concentrations measured by the instruments lie within the bounds established by their estimated uncertainty as determined by the principal investigator and based on the basic physical and chemical process that defines the instrument operation.

RECOMMENDATIONS

Based on workshop discussions and the material presented in this document, recommendations are presented in four areas:

1. Current instrument technology advances

2. Future instrument needs

3. Promising new technology

4. Measurement validation

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Each recommendation is presented as a work area that, if pursued, would improve measurement capabilities for N_xO_y species at "clean" global concentrations. Each recommendation has been discussed earlier and is therefore only summarized here. It was the decision of the N_xO_y workshop participants not to place a priority on the recommendations relative to their potential for improving measurement capabilities.

Current Instrumentation Technology Advances

As stated earlier, field techniques are or in the near future will be available for measurement of NO, NO_2, HNO_3, and NO_3^- aerosols at tropospheric levels. Techniques for NO_3, HNO_2, and PAN show potential but appear to lack the necessary programmatic and scientific interest to conclude that these techniques will be available. In any case, associated with each technique are uncertainties, limitations, or known improvements which require additional study or implementation if the full potential of the technique is to be realized. In most cases either hardware redesign or subcomponent development is the required technology advance. These technology advances and recommendations are summarized by technique.

1. NO/O_3 Chemiluminescence (NO, NO_2, HNO_3):

   (a) Redesign of photon collection and detection systems

   (b) Intercomparison among photolytic, pyrolytic, catalytic, and denuder-tube conversion techniques for species other than NO

2. Single-Photon Laser-Induced Fluorescence (NO): Development of an improved laser at 226 nm; higher energy per pulse and higher repetition rates

3. Tunable-Diode Laser (NO, NO_2, HNO_3):

   (a) Development of more stable and higher energy diode lasers

   (b) Improved refrigeration techniques suitable for field use

   (c) Redesign of optical systems

4. Long-Path Absorption (NO, NO_2, HNO_2, NO_3):

   (a) Development of higher intensity light sources

   (b) Development of larger collection optics

5. Filter (NO_3^- aerosol, HNO_3): Improvement in analysis sensitivities of ion chromatography

6. Condensation (HNO_2, HNO_3):

   (a) Improvement in analysis sensitivities of ion chromatography

   (b) Development of a flow-through sample configuration

7. Gas Chromatography (PAN):

   (a) Redesign of system for rugged field use

   (b) Improvements in calibration procedures and standard preparation

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Future Instrument Needs

It was a consensus that measurement techniques for N_2O_5 and HNO_4 are nonexistent for use onboard an aircraft. Assuming that the atmospheric modeling community identifies these as important species, then instrument concepts need to be developed.

It was noted that for some species (for example, NO_3, HNO_2, and PAN) only a few concepts are being developed. Most of these techniques are indirect methods of measurement and historically have sizeable systemic errors. Development of additional techniques for these species, based on different concepts (direct measurement where possible) will provide more credibility and help ensure acceptance by the scientific community.

Two areas of fundamental research are recommended. Both are areas which, in the opinion of the N_xO_y workshop participants, are limiting the potential of many techniques for measurement of N_xO_y species. In addition, both areas were judged to be equally important in tropospheric air quality measurements in general. The first area is calibration standards and procedures. With the exception of NO and NO_2, accepted calibration standards and procedures for other N_xO_y species are nonexistent. Even for NO and NO_2, the accepted procedures are for calibration at ppmv levels, whereas field measurements are being attempted at pptv and ppbv levels. It is recommended that fundamental research be initiated to attempt to extend calibration and standards preparation to the ppbv and pptv levels.

The second area of fundamental research is laser development. Most participants agreed that fundamental improvements in lasers would improve the measurement capabilities of the laser-based detection systems. Laser improvements desired included higher energy lasers with higher repetition rates, more options in available wavelengths, longer lifetimes, and more rugged design for use on aircraft platforms.

Promising New Technologies

Several new technologies were identified as exhibiting potential for measurement of the various N_xO_y species (Tables V to XI, status 1 or 2). It is recommended that the development of these new technologies be continued where possible, especially for those species for which only a few measurement concepts or indirect measurement concepts exist. Promising laser techniques include laser-induced fluorescence (single photon, two photon, and photofragmentation), multiphoton ionization, and resonant ionization spectroscopy. These techniques show potential for high-sensitivity and fast-response measurements and also provide the specificity of a direct and spectroscopic technique. Other techniques that show promise include the tungstic-acid, condensation, and photothermal (photoacoustic phase fluctuation optical heterodyne) techniques. These three techniques, although not new, have not been developed to their full potential.

Measurement Validation

The recommendation in this area is that more effort should be focused on measurement validation and intercomparison among techniques measuring the same species. In the final analysis, the criterion by which the accuracy of the measurement of an atmospheric species is established is intercomparison of measurements made by instruments using different principles of detection. Such measurements are carried out in the field and are subjected to a wide variety of atmospheric concentrations. Prerequisites for field intercomparisons are instrument calibrations using validated procedures and traceable standards.

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16. Abstract

In its continuing efforts to direct its applications programs towards relevant national needs, NASA is conducting the Tropospheric Chemistry Program, the long-range objective of which is to apply NASA's space technology to assess and predict human impact on the troposphere, particularly on the regional to global scale. One area of required research is instrumentation development, which is aimed at improving the capability to measure important trace gases and aerosols which are key species in the major atmospheric biogeochemical cycles. To focus on specific needs, the Instrumentation Workshop for N_xO_y Tropospheric Species was conducted in August 1982. The workshop discussed current measurement needs and instrument capabilities for N_xO_y species, including NO, NO_2, HNO_3, HNO_2, PAN, and NO_3^- aerosols. The status and measurement capabilities of various techniques (operational as well as conceptual) were discussed, along with future instrument and technology needs. This report documents the workshop activities and conclusions.

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